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### SNI

Ciencias Naturales y Exactas / Ciencias Químicas  
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## Datos Generales

### INSTITUCIÓN PRINCIPAL

Universidad de la República/ Facultad de Química / CCBG - DETEMA / Uruguay

### DIRECCIÓN INSTITUCIONAL

Institución: Universidad de la República / Facultad de Química / Sector Educación Superior/Público / CCBG-DETEMA

Dirección: Avda. Gral. Flores 2124 / 11800

País: Uruguay / Montevideo / Montevideo

Teléfono: (598) 29248396

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## Formación

### Formación académica

#### CONCLUIDA

#### DOCTORADO

##### Doctorado (1991 - 1995)

Universität Heidelberg (Ruprecht-Karls), Alemania

Título de la disertación/tesis/defensa: Theoretische Untersuchungen an chemischen und biochemischen Subsystemen zu Struktur und Funktion Chemischer Nukleasen

Tutor/es: Sandor Suhai

Obtención del título: 1995

Financiación:

Heidelberg University, Alemania

Palabras Clave: Nucleasas Biología Computacional Biofísica Química Teórica

Áreas de conocimiento:

Ciencias Naturales y Exactas / Ciencias Químicas / Físico-Química, Ciencia de los Polímeros, Electroquímica / Química Teórica y Computacional

#### MAESTRÍA

##### Diplom-Chemiker (1985 - 1990)

Universität Stuttgart, Alemania

Título de la disertación/tesis/defensa: Absorptions- und Emissionsspektroskopische Untersuchungen an UV-Stabilisatoren des ortho-Hydroxyphenyl-Triazin-Typs

Tutor/es: H. E. A. Kramer

Obtención del título: 1991

Financiación:

Universität Stuttgart, Alemania

Palabras Clave: Espectroscopía UV-Vis Fluorescencia Estabilizadores UV Triazinas

Áreas de conocimiento:

Ciencias Naturales y Exactas / Ciencias Químicas / Físico-Química, Ciencia de los Polímeros, Electroquímica / Espectroscopía

#### GRADO

##### Vordiplom (1981 - 1985)

Universität Stuttgart, Alemania

Título de la disertación/tesis/defensa:

Obtención del título: 1985

Áreas de conocimiento:

Ciencias Naturales y Exactas / Ciencias Químicas / Físico-Química, Ciencia de los Polímeros, Electroquímica /

## EN MARCHA

### PREGRADO

#### Secundaria (1975)

Albert-Schweitzer-Gymnasium ,Alemania

Título de la disertación/tesis/defensa:

Palabras Clave: Secundaria

Áreas de conocimiento:

Ciencias Naturales y Exactas / Ciencias Químicas / Físico-Química, Ciencia de los Polímeros, Electroquímica /

## Formación complementaria

## CONCLUIDA

### POSDOCTORADOS

#### Estudios de radicales empleando métodos de funcionales de la densidad (1996 - 1999)

Sector Educación Superior/Público / Universidad de la República / Facultad de Química , Uruguay

Palabras Clave: Química Teórica Radicales Funcionales de la densidad

Áreas de conocimiento:

Ciencias Naturales y Exactas / Ciencias Químicas / Físico-Química, Ciencia de los Polímeros, Electroquímica / Química Teórica y Computacional

### CURSOS DE CORTA DURACIÓN

#### Coarse-grained Simulation of Biological Soft Matter Systems using ESPResSo (01/2011 - 01/2011)

Sector Extranjero/Internacional/Otros / Universität Stuttgart , Alemania

40 horas

Palabras Clave: Química computacional software

Áreas de conocimiento:

Ciencias Naturales y Exactas / Ciencias Químicas / Físico-Química, Ciencia de los Polímeros, Electroquímica / Química Teórica y Computacional

### PARTICIPACIÓN EN EVENTOS

#### scientific meeting with Dr. Tilman Kottke, Bielefeld (2017)

Tipo: Seminario

Institución organizadora: Physikalische Chemie III, Bielefeld, Alemania

Palabras Clave: Flavin-Adenosin-Dinucleotide UV y IR-Spectra DFT T-DFT

#### Scientific Meeting with Dr. Luise Krauth-Siegel (2013)

Tipo: Taller

Institución organizadora: Biochemistry Center, University of Heidelberg, Alemania

Palabras Clave: Leishmaniasis Computational enzymology

Áreas de conocimiento:

Ciencias Naturales y Exactas / Ciencias Químicas / Físico-Química, Ciencia de los Polímeros, Electroquímica / Química Teórica y Computacional

### OTRAS INSTANCIAS

#### Estudio de las Matemáticas (Bachelor of Sciences): Modelización matemática en física (2018)

Alemania

Palabras Clave: Matemática Modelización matemática en física New DFT-potentials

Áreas de conocimiento:

Ciencias Naturales y Exactas / Ciencias Químicas / Ciencias Químicas / química teorica

## Idiomas

### Inglés

Entiende muy bien / Habla muy bien / Lee muy bien / Escribe muy bien

### Alemán

Entiende muy bien / Habla muy bien / Lee muy bien / Escribe muy bien

### Español

Entiende muy bien / Habla regular / Lee muy bien / Escribe bien

### Francés

Entiende bien / Habla bien / Lee bien / Escribe bien

### Latín

Entiende regular / Habla regular / Lee regular / Escribe regular

## Áreas de actuación

### CIENCIAS NATURALES Y EXACTAS

Ciencias Químicas / Físico-Química, Ciencia de los Polímeros, Electroquímica / Química Teórica y Computacional

## Actuación profesional

**SECTOR EDUCACIÓN SUPERIOR/PÚBLICO - UNIVERSIDAD DE LA REPÚBLICA - URUGUAY**

Facultad de Química / CCBG-DETEMA

### VÍNCULOS CON LA INSTITUCIÓN

#### **Funcionario/Empleado (01/2017 - a la fecha)** Trabajo relevante

340 horas semanales

Escalafón: Docente

#### **Funcionario/Empleado (01/2012 - 12/2016)** Trabajo relevante

Profesor Adjunto 40 horas semanales

Escalafón: Docente

Grado: Grado 3

Cargo: Efectivo

### ACTIVIDADES

#### DOCENCIA

##### **Fisicoquímica Molecular Básica (01/2017 - a la fecha)**

Grado

Responsable

Asignaturas:

detema, 40 horas, Teórico-Práctico

Áreas de conocimiento:

Ciencias Naturales y Exactas / Ciencias Químicas / Ciencias Químicas / química cuantica

##### **Carreras de Facultad de Química (01/2012 - 12/2016)**

Grado

Asistente

Asignaturas:

Fisicoquímica Molecular Básica, 6 horas, Teórico-Práctico

Áreas de conocimiento:

Ciencias Naturales y Exactas / Ciencias Químicas / Físico-Química, Ciencia de los Polímeros, Electroquímica / Química Teórica y Computacional

**SECTOR EDUCACIÓN SUPERIOR/PÚBLICO - UNIVERSIDAD DE LA REPÚBLICA - URUGUAY**

Facultad de Química / detema

#### VÍNCULOS CON LA INSTITUCIÓN

##### **Funcionario/Empleado (12/2002 - 12/2011)**

Profesor Adjunto 40 horas semanales  
Escalafón: Docente  
Grado: Grado 3  
Cargo: Efectivo

##### **Funcionario/Empleado (08/2001 - 12/2002)**

Profesor Adjunto 40 horas semanales  
Escalafón: Docente  
Grado: Grado 3  
Cargo: Interino

##### **Funcionario/Empleado (08/1999 - 07/2001)**

Profesor Agregado CSIC 40 horas semanales  
Programa de Científicos Provenientes del exterior de la CSIC, Cátedra de Química Cuántica, Facultad de Química, Universidad de la República.  
Escalafón: Docente  
Grado: Grado 4  
Cargo: Interino

#### ACTIVIDADES

##### LÍNEAS DE INVESTIGACIÓN

##### **Funcionales de la Densidad (12/2006 - 12/2015 )**

Uso y validación de los métodos de funcionales de la densidad para el estudio de la estructura y reactividad de pequeñas moléculas orgánicas e inorgánicas, en particular moléculas que contienen azufre y halógenos. Determinación de propiedades termoquímicas, en particular calores de formación mediante el uso de reacciones isodérmicas.  
15 horas semanales  
DETEMA, CCBG, Integrante del equipo  
Equipo: ON VENTURA, M. E. SEGOVIA  
Palabras clave: Química Teórica Métodos de Funcionales de la Densidad Termoquímica Computacional  
Areas de conocimiento:  
Ciencias Naturales y Exactas / Ciencias Químicas / Físico-Química, Ciencia de los Polímeros, Electroquímica / Química Teórica y Computacional

##### **Biomiméticos (11/2006 - 12/2015 )**

Estudios de complejos de metales de transición en interacción con aminoácidos y macrociclos que simulan el comportamiento de sitios activos de enzimas. Empleo de métodos de funcionales de la densidad y de dinámica molecular (QM/MM) para la determinación de estructura y reactividad, en particular de complejos que involucran aminoácidos azufrados (cisteína y homocisteína) en particular relacionados con la importancia metabólica de la homocisteína.  
15 horas semanales  
DETEMA, CCBG, Coordinador o Responsable  
Equipo: ON VENTURA  
Palabras clave: Métodos de Funcionales de la Densidad Enzimas Biomiméticos Complejos de Metales de Transición  
Areas de conocimiento:  
Ciencias Naturales y Exactas / Ciencias Químicas / Físico-Química, Ciencia de los Polímeros, Electroquímica / Química Teórica y Computacional

**Nanotransductores en procesos celulares de señales redox efectuadas por especies reactivas de**

**oxígeno. Óxido-reducción de residuos con azufre y selenio en proteínas, inhibidores y biomiméticos involucrados en los procesos de regulación redox (01/2010 - 06/2015 )**

La propuesta consiste en apuntalar diversas líneas de investigación convergentes en un programa de enzimología computacional. Si bien el programa se plantea para financiamiento a 48 meses, las previsiones de equipamiento, formación de capital computacional y recursos humanos, dentro de una temática novedosa y relativamente poco desarrollada, apunta a un programa a largo plazo (10-15 años) donde naturalmente las líneas de investigación irán mutando de acuerdo al conocimiento generado. El centro temático de la propuesta es el funcionamiento de ROS, específicamente H<sub>2</sub>O<sub>2</sub> como mensajero secundario que afecta la actividad y conformación de enzimas involucradas en la reparación de oxidación de proteínas. Las enzimas a estudiarse funcionan todas por oxidación de azufre a disulfuro, sulfóxidos, sulfenos, sulfinos, sulfonas (y las especies equivalentes para selenio). No todas las enzimas involucradas en el proceso de oxidación de tioles van a ser investigadas en este programa, sino que se eligieron algunas en particular, que presentan características interesantes y novedosas. Desde el punto de vista temático, el interés de este proyecto descansa en dos aspectos. Por un lado, el hecho de que para las enzimas que proponemos estudiar, los mecanismos de acción detallados, así como las variables fisicoquímicas que los afectan no son completamente conocidas a nivel molecular. Por otro lado, el estudio de inhibidores y biomiméticos nos permite una aproximación biotecnológica hacia la fabricación de enzimas artificiales para actuar, por ejemplo, como antioxidantes sintéticos o reaccionar a las señales de aumento de concentración de H<sub>2</sub>O<sub>2</sub>. Las siguientes son las líneas de investigación. a) Desarrollo de software de bioinformática estructural. b) Investigación de reacciones químicas en medio acuoso a distintos pH, para determinar estructuras, interacciones, espectros y propiedades energéticas de las reacciones orgánicas que están en el centro del proceso catalítico, pero realizadas sobre modelos en solución acuosa. c) Investigación de reactivos para reconocimiento de sulfinos y sulfonas, para intentar obtener compuestos que reaccionen más fácilmente con estos que con sulfenos, para usar como reactivos de reconocimiento específico. d) Investigación sobre biomiméticos, moléculas simples (complejos metálicos o macrociclos orgánicos) que mimiten la acción de la Gpx. e) Investigaciones sobre complejos metálicos de Cys, HCys y Sec, para entender el efecto catalítico de los iones Zn<sup>+2</sup> y Cu<sup>+2</sup> en interacción con los tioles, y cómo modifica esta interacción la oxidabilidad de los tioles (o selenoles) unidos a él. f) Investigaciones sobre PTP1B (fosforilación y oxidación por H<sub>2</sub>O<sub>2</sub>) para entender su inactivación reversible e irreversible, en particular en sus reacciones con H<sub>2</sub>O<sub>2</sub>, investigando su estabilidad en el tiempo mediante cálculos QM/MM de dinámica molecular. g) Investigaciones sobre el complejo peroxiredoxina/sulfiredoxina para comprender la importancia de la transformación sulfénico/sulfinico como señal celular y de qué manera se evita la inactivación irreversible. h) Investigaciones sobre Betaína-homocisteína S-metiltransferasa y Methiona-R-sulfóxido reductasas para determinar las estructuras y la energética del mecanismo de transferencia de metilo a la HCys, la oxidación de Met a MetSo y la reducción enantiomérica de la misma, considerando la diferencia de eficiencia entre Cys y Sec. i) Investigaciones sobre mutación de Cys con HCys y Sec.

20 horas semanales

Facultad de Química, CCBG, DETEMA, Integrante del equipo

Equipo: ON VENTURA, K. IRVING, M. SEGOVIA, F. BOTTINELLI, BERMUDEZ, E., SAENZ-MENDEZ, P., VEGA-TEIJIDO, M., KATZ, A.

Palabras clave: Química computacional bioquímica computacional tioles Enzimología computacional

Áreas de conocimiento:

Ciencias Naturales y Exactas / Ciencias Químicas / Físico-Química, Ciencia de los Polímeros, Electroquímica / Química Teórica y Computacional

**PROYECTOS DE INVESTIGACIÓN Y DESARROLLO**

**Production and extraction of high value chemicals through the oxidation of lignin in supercritical CO<sub>2</sub> (05/2007 - 05/2009 )**

5 horas semanales

DETEMA, CCBG

Investigación

Integrante del Equipo

Concluido

Alumnos encargados en el proyecto:

Pregrado:1

Equipo: ON VENTURA (Responsable), K. IRVING, P. SAENZ, I. JACHMANIAN, D. GONZÁLEZ, V. ALDABALDE

**Estudio computacional de la activación de oxígeno molecular en complejos mono y binucleares de Fe y Cu con importancia biológica (03/2000 - 02/2002 )**

20 horas semanales  
Dequifim , Cátedra de Química Cuántica  
Investigación  
Coordinador o Responsable  
Concluido  
Equipo: ON VENTURA , K. IRVING

**Estudios de radicales empleando métodos de funcionales de la densidad (12/1996 - 12/1998 )**

20 horas semanales  
Dequifim , Cátedra de Química Cuántica  
Investigación  
Integrante del Equipo  
Concluido  
Financiación:  
Institución del exterior, Beca  
Equipo: ON VENTURA (Responsable)  
Areas de conocimiento:  
Ciencias Naturales y Exactas / Ciencias Químicas / Físico-Química, Ciencia de los Polímeros,  
Electroquímica / Química Teórica y Computacional

**DOCENCIA**

**Doctorado en Química (11/2006 - 12/2012 )**

Doctorado  
Responsable  
Asignaturas:  
Química Computacional, 6 horas, Teórico-Práctico  
Areas de conocimiento:  
Ciencias Naturales y Exactas / Ciencias Químicas / Físico-Química, Ciencia de los Polímeros,  
Electroquímica / Química Teórica y Computacional

**SECTOR EXTRANJERO/INTERNACIONAL/OTROS - ALEMANIA**

German Cancer Research Center

**VÍNCULOS CON LA INSTITUCIÓN**

**Otro (01/1996 - 11/1996)**

Científico Contratado 20 horas semanales

**Funcionario/Empleado (01/1991 - 12/1995)**

BAT 2A/2 20 horas semanales  
Tutor sobre computación y programación de los estudiantes de doctorado del Prof. Dr. Sandor Suhai, Proyecto NEUROGEN.

**SECTOR EXTRANJERO/INTERNACIONAL/OTROS - ALEMANIA**

Universität Stuttgart

**VÍNCULOS CON LA INSTITUCIÓN**

**Colaborador (01/1990 - 12/1991)**

Asistente Científico Ins. Físicoquímica 10 horas semanales  
Tutoría de estudiantes de grado en Química Orgánica.

**SECTOR EXTRANJERO/INTERNACIONAL/OTROS - ALEMANIA**

# Institut zur Steuerung von Werkzeugmaschinen

## VÍNCULOS CON LA INSTITUCIÓN

### **Funcionario/Empleado (01/1989 - 12/1990)**

Programador 20 horas semanales  
Programador para el Instituto de Robótica

### **SECTOR EXTRANJERO/INTERNACIONAL/OTROS - ALEMANIA**

## Bischoff-Analysen-Geräte

## VÍNCULOS CON LA INSTITUCIÓN

### **Funcionario/Empleado (01/1982 - 12/1983)**

Control de Calidad 20 horas semanales  
Control de calidad de columnas para HPLC

### **CARGA HORARIA**

Carga horaria de docencia: 6 horas  
Carga horaria de investigación: 30 horas  
Carga horaria de formación RRHH: 2 horas  
Carga horaria de extensión: Sin horas  
Carga horaria de gestión: 2 horas

## Producción científica/tecnológica

La aparición de computadoras cada vez más potentes y veloces ha llevado a que el modelado molecular (es decir, la aplicación de métodos físico-matemáticos de la química teórica al estudio de sistemas atómicos y moleculares de importancia en química y biología) se transforme en una técnica estándar de investigación científica. La química computacional es la variante más sofisticada del modelado molecular y comprende el desarrollo, validación y testeo de modelos de cálculo para identificar sus fortalezas y debilidades en el cálculo de propiedades moleculares.

Mi labor de investigación científica se ha centrado en el estudio de modelos de sistemas de importancia en biología, desde fragmentos que simulan enlaces peptídicos (formamida) o aminoácidos concretos (glicina, cisteína) hasta moléculas mucho más grandes y complicadas (DNA antisentido, por ejemplo). Desde el punto de vista metodológico mis contribuciones se han centrado en el estudio de enlaces de hidrógeno, problemas de solvatación, problemas conformacionales, determinación de entalpías de reacción y de formación, y estructura y reactividad de moléculas orgánicas y complejos de metales de transición, en un intento de atacar el problema de los biomiméticos. Un capítulo especial ha sido el estudio de radicales libres, que son por un lado importantes en distintos problemas biológicos y, por otro, son normalmente difíciles de describir con los métodos convencionales de la química computacional, por lo cual su estudio con métodos de funcionales de la densidad ameritó una relativamente extensa investigación.

Algunos de los artículos publicados han conseguido un alto impacto, en particular los relacionados con el tratamiento incorrecto del enlace de hidrógeno hecho por los métodos DFT o, por el contrario, el clamoroso éxito obtenido por estos métodos en el estudio de problemas termoquímicos de moléculas que presentan enlaces covalentes entre átomos de alta electronegatividad (como F y O, por ejemplo).

En el presente, la investigación ha sido reorientada hacia el estudio de complejos de metales de transición que mimeticen centros activos de enzimas, con énfasis en la interacción teórico-experimental. Estoy contribuyendo especialmente en el estudio de los complejos de tioles biológicos con Zn y se han publicado dos artículos en 2010 y 2011 en los cuales se reportan aspectos parciales de estos estudios. En un caso se trata del reconocimiento estructural y espectroscópico del complejo de Zn con cisteínas en solución acuosa y en el otro se trata de la espectroscopía de los tioles simples en fase gaseosa y en su interacción con agua. Estos estudios sirven de base para la investigación que se está realizando en 2011, donde se trabaja en la interacción de sulfuros con un complejo pirazolyl borato Zn (comunicado al congreso WATOC en España y SBQT en Brasil), la reacción de peróxido con un derivado de cisteína (en marcha) y la

conversión de cisteína complejada con Zn en ácido sulfénico o cistina. Paralelamente, me desempeño como la mano derecha del prof. Oscar Ventura en sus estudios sobre química atmosférica donde hemos publicado varios artículos en los últimos años y hemos iniciado una colaboración con el prof. Ricardo Faccio sobre absorción de compuestos biológicos en superficies de MXenos.

## Producción bibliográfica

### ARTÍCULOS PUBLICADOS

#### ARBITRADOS

##### **Electronic properties of L-tryptophan adsorbed on Ti<sub>3</sub>C<sub>2</sub>T<sub>x</sub> (T=O) MXenes (Completo, 2023)**

FERNÁNDEZ-WERNER, L., ESTEVES, M., AMY, L., M. KIENINGER, VENTURA, O.N., FACCIIO, R. MRS Advances, v.: 2023 2023

Palabras clave: Mexenes two dimensional materials triptofano absorcion espectro electrónico

Areas de conocimiento:

Ciencias Naturales y Exactas / Ciencias Físicas / Física Atómica, Molecular y Química / Química del estado sólido

Ciencias Naturales y Exactas / Ciencias Químicas / Físico-Química, Ciencia de los Polímeros, Electroquímica / Espectroscopías

Medio de divulgación: Papel

E-ISSN: 20598521

DOI: <https://doi.org/10.1557/s43580-023-00655-6>

<https://link.springer.com/article/10.1557/s43580-023-00655-6>

MXenes are the largest graphene like two-dimensional material family developed in recent years. They exhibit unique layered structures with outstanding physical and chemical properties, which can be tunable varying the surfaces terminal groups. In this article, the effect of oxygen saturation on the reactivity of Ti<sub>3</sub>C<sub>2</sub> surfaces is evaluated by means of first-principles modeling of Ti<sub>3</sub>C<sub>2</sub>O<sub>x</sub>=1 or 2 slabs. Both surfaces exhibit metallic character and work functions show larger reactivity in the case of superficial oxygen deficiency. To further evaluate the surface reactivity, the amino acid model L-tryptophan was studied. The stable configurations of the adsorbed molecule were obtained, and the more stable adducts were found for Ti<sub>3</sub>C<sub>2</sub>O. In the case of Ti<sub>3</sub>C<sub>2</sub>O<sub>2</sub>, physisorption occurs while in the case of Ti<sub>3</sub>C<sub>2</sub>O, dissociative bidentate chemisorption configuration is adopted. Differences in optical absorbance and work function energy were determined as a preliminary step towards the evaluation of these structures as potential sensing devices.

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##### **SVECV-f12: A composite scheme for accurate and cost-effective evaluation of reaction barriers. II. Benchmarking using Karton's BH28 barrier heights database (Completo, 2023)**

M. KIENINGER, VENTURA, O.N.

International Journal of Quantum Chemistry, v.: 123 24, 2023

Palabras clave: métodos compuestos energías de reacción barreras de reacción métodos de funcionales de la densidad ccsd(t)-f12

Areas de conocimiento:

Ciencias Naturales y Exactas / Ciencias Químicas / Físico-Química, Ciencia de los Polímeros, Electroquímica / Química computacional

Medio de divulgación: Papel

ISSN: 00207608

E-ISSN: 1097461X

DOI: <https://doi.org/10.1002/qua.27069>

<https://onlinelibrary.wiley.com/doi/abs/10.1002/qua.27069>

A simple composite scheme developed for the calculation of accurate reaction barriers, and benchmarked against small systems, is applied here to compute barriers in the BH28 data set published in 2019 by Karton. This set comprises more complex transition states, with up to 7 non-hydrogen and 10 hydrogen atoms, which barriers calculated at the SVECV-f12 level are compared to the accurate CCSDT(Q)/CBS values obtained by Karton. A mean absolute difference of 2.4 kJ mol<sup>-1</sup> and a root mean square difference of 1.9 kJ mol<sup>-1</sup> were obtained, underlying the chemical accuracy of the protocol.

Scopus® WEB OF SCIENCE™

##### **Accuracy of enthalpies of formation of hydrocarbons using the SVECV-f12 protocol and comparison to**

#### **other composite methods (Completo, 2023)**

VEGA-TEIJIDO MA, MARC SEGOVIA, M. KIENINGER, VENTURA, O.N.

The Journal of Chemical Thermodynamics, v.: 189 2023

Palabras clave: hidrocarburos energías de atomización calores de formación métodos compuestos

Areas de conocimiento:

Ciencias Naturales y Exactas / Ciencias Químicas / Físico-Química, Ciencia de los Polímeros, Electroquímica / Química computacional

Medio de divulgación: Papel

ISSN: 00219614

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DOI: <https://doi.org/10.1016/j.jct.2023.107197>

<https://www.sciencedirect.com/science/article/abs/pii/S0021961423001945>

A recently developed composite chemical model, SVECV-f12, intended for a simple and accurate reproduction of barrier heights, is used to determine the energies of atomization and enthalpies of formation of 27 hydrocarbon species included in the W4-17 dataset. The values are compared to the highly accurate W4 theoretical values on one side, and to the enthalpies of formation in the Active Thermochemical Tables on the other. In both cases it is found that there is systematic error which can be easily corrected by a linear correlation. After correction, an r.m.s. deviation of 3.60 kJ mol<sup>-1</sup> was obtained with respect to the W4 values, and 3.48 kJ mol<sup>-1</sup> with respect to the ATcT values. The procedure was then applied to cases in which a large deviation exists between experimental and theoretical data in the literature, further applied to the prediction of the enthalpy of formation of other hydrocarbons which experimental values are unknown, as well as to obtaining hydrogenation and isomerization enthalpies for small-size hydrocarbons.

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#### **Degradation mechanism of 2-fluoropropene by Cl atoms: experimental and theoretical products distribution studies (Completo, 2022)**

RIVELA, CB, CARDONA; AL, BLANCO, MB, BARNES, I, M. KIENINGER, VENTURA, O.N., TERUEL, MA

Physical Chemistry Chemical Physics, v.: 24 p.:5094 - 5108, 2022

Palabras clave: 2-fluoropropene oxidation atmospheric chemistry density functional methods reaction mechanisms

Areas de conocimiento:

Ciencias Naturales y Exactas / Ciencias Químicas / Físico-Química, Ciencia de los Polímeros, Electroquímica / Química Computacional

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The gas-phase reaction products of 2-fluoropropene (2FP) with Cl atoms have been determined for the first time at 298 K and atmospheric pressure using a 1080 L quartz-glass photoreactor coupled with in situ FTIR spectroscopy to monitor reactants and products. Acetyl fluoride and formyl chloride were observed as the main products with yields of (106 ± 10)% and (100 ± 11)%, respectively. Electronic structure calculations of reactants, intermediates, products and transition states on a detailed mechanism of the reaction were performed by DFT procedures (BMK, M06, M062X/D3), as well as accurate composite methods on both the addition and abstraction reaction channels. From the joint experimental and theoretical studies, we concluded that the reaction occurs primarily via addition to the C<sup>β</sup> carbon, with a smaller participation of the addition on the C<sup>α</sup> carbon, which is not produced directly from the separated reactants but from the CH<sub>3</sub>CFCH<sub>2</sub>Cl intermediate radical through a submerged transition state. The abstraction channel occurs at larger energies than the addition ones, and also presents a submerged transition state, with a lower barrier. No products arising from this channel are expected. The proposed mechanism explains also why formaldehyde, predicted as a product by former theoretical studies, is not found among the experimental products. The atmospheric implications of the reaction products are assessed.

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#### **Correcting the Experimental Enthalpies of Formation of Some Members of the Biologically Significant Sulfenic Acids Family (Completo, 2022)**

VENTURA, O.N., MARC SEGOVIA, VEGA-TEIJIDO MA, KATZ, A., M. KIENINGER, TASINATO, N, SALTA, Z

The Journal of Physical Chemistry A, v.: 126 36, p.:6091 - 6109, 2022

Palabras clave: sulfenic acids composite methods heats of formation density functional methods experimental correction

Areas de conocimiento:

Ciencias Naturales y Exactas / Ciencias Químicas / Físico-Química, Ciencia de los Polímeros, Electroquímica / Química computacional

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Sulfenic acids are important intermediates in the oxidation of cysteine thiol groups in proteins by reactive oxygen species. The mechanism is influenced heavily by the presence of polar groups, other thiol groups, and solvent, all of which determines the need to compute precisely the energies involved in the process. Surprisingly, very scarce experimental information exists about a very basic property of sulfenic acids, the enthalpies of formation. In this Article, we use high level quantum chemical methods to derive the enthalpy of formation at 298.15 K of methane-, ethene-, ethyne-, and benzenesulfenic acids, the only ones for which some experimental information exists. The methods employed were tested against well-known experimental data of related species and extensive CCSD(T) calculations. Our best results consistently point out to a much lower enthalpy of formation of methanesulfenic acid,  $\text{CH}_3\text{SOH}$  ( $\Delta_f H^\circ(298.15\text{K}) = -35.1 \pm 0.4 \text{ kcal mol}^{-1}$ ), than the one reported in the NIST thermochemical data tables. The enthalpies of formation derived for ethynesulfenic acid,  $\text{HC}\equiv\text{CSOH}$ ,  $+32.9 \pm 1.0 \text{ kcal/mol}$ , and benzenesulfenic acid,  $\text{C}_6\text{H}_5\text{SOH}$ ,  $-2.6 \pm 0.6 \text{ kcal mol}^{-1}$ , also differ markedly from the experimental values, while the enthalpy of formation of ethenesulfenic acid  $\text{CH}_2\text{CHSOH}$ , not available experimentally, was calculated as  $-11.2 \pm 0.7 \text{ kcal mol}^{-1}$ .

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### **Correcting the Experimental Enthalpies of Formation of Some Members of the Biologically Significant Sulfenic Acids Family (Completo, 2022)**

VENTURA, O.N., MARC SEGOVIA, VEGA-TEIJIDO MA, KATZ, A., M. KIENINGER, TASINATO, N, SALTA, Z

The Journal of Physical Chemistry A, v.: 126 36, p.:6091 - 6109, 2022

Palabras clave: sulfenic acids composite methods heats of formation density functional methods experimental correction

Areas de conocimiento:

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Sulfenic acids are important intermediates in the oxidation of cysteine thiol groups in proteins by reactive oxygen species. The mechanism is influenced heavily by the presence of polar groups, other thiol groups, and solvent, all of which determines the need to compute precisely the energies involved in the process. Surprisingly, very scarce experimental information exists about a very basic property of sulfenic acids, the enthalpies of formation. In this Article, we use high level quantum chemical methods to derive the enthalpy of formation at 298.15 K of methane-, ethene-, ethyne-, and benzenesulfenic acids, the only ones for which some experimental information exists. The methods employed were tested against well-known experimental data of related species and extensive CCSD(T) calculations. Our best results consistently point out to a much lower enthalpy of formation of methanesulfenic acid,  $\text{CH}_3\text{SOH}$  ( $\Delta_f H^\circ(298.15\text{K}) = -35.1 \pm 0.4 \text{ kcal mol}^{-1}$ ), than the one reported in the NIST thermochemical data tables. The enthalpies of formation derived for ethynesulfenic acid,  $\text{HC}\equiv\text{CSOH}$ ,  $+32.9 \pm 1.0 \text{ kcal/mol}$ , and benzenesulfenic acid,  $\text{C}_6\text{H}_5\text{SOH}$ ,  $-2.6 \pm 0.6 \text{ kcal mol}^{-1}$ , also differ markedly from the experimental values, while the enthalpy of formation of ethenesulfenic acid  $\text{CH}_2\text{CHSOH}$ , not available experimentally, was calculated as  $-11.2 \pm 0.7 \text{ kcal mol}^{-1}$ .

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### **SVECV-f12: Benchmark of a composite scheme for accurate and cost effective evaluation of reaction barriers (Completo, 2021)**

VENTURA, O.N., M. KIENINGER, KATZ, A., VEGA-TEIJIDO MA, MARC SEGOVIA, K. IRVING  
International Journal of Quantum Chemistry, v.: 121 18, p.:26745 2021

Palabras clave: composite methods density functional methods barriers of reaction CCSD(T)-F12

Areas de conocimiento:

Ciencias Naturales y Exactas / Ciencias Químicas / Físico-Química, Ciencia de los Polímeros,

Electroquímica / Química computacional

Medio de divulgación: Papel

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A simple composite scheme is presented and benchmarked against the 38 reactions in Truhlar's HTBH38/08 and NHTBH38/08 databases. Mean unsigned deviation (MUD) for the complete set of 68 independent barriers is 0.40 kcal mol<sup>-1</sup>, compared to 1.31 kcal mol<sup>-1</sup> for G4 and 1.62 kcal mol<sup>-1</sup> for the M06-2X-D3 method. The MUD of the new scheme on the barriers in the DBH24/08 subset (12 out of the 38 reactions in the other sets) is 0.27 kcal mol<sup>-1</sup>, better than that obtained at the expensive CCSD(T,full)/aug-cc-pCV(T+d)Z level (0.46 kcal mol<sup>-1</sup>) and comparable to the most exact (and costly) Wn calculations (MUD = 0.14 kcal mol<sup>-1</sup>). The method was further tested against a subset of reactions, for which the geometry and energies of all species were determined at the much more demanding CCSD(T)-F12//pVQZ-F12 level. The SVECV-f12 procedure on this database results in RMSE and MUD values of only 0.21 and 0.16 kcal mol<sup>-1</sup>.

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### **Calculation of the Geometries and Infrared Spectra of the Stacked Cofactor Flavin Adenine Dinucleotide (FAD) as the Prerequisite for Studies of Light-Triggered Proton and Electron Transfer (Completo, 2020)**

M. KIENINGER, VENTURA, O.N., KOTTKE, T

Biomolecules, v.: 10 4, p.:573 2020

Palabras clave: stacked flavin adenine dinucleotide FAD microsolvation vibrational spectroscopy supramolecular orbitals

Areas de conocimiento:

Ciencias Naturales y Exactas / Ciencias Químicas / Físico-Química, Ciencia de los Polímeros,

Electroquímica / Química computacional

Medio de divulgación: Internet

E-ISSN: 2218273X

DOI: <https://doi.org/10.3390/biom10040573>

<https://www.mdpi.com/2218-273X/10/4/573>

Flavin cofactors, like flavin adenine dinucleotide (FAD), are important electron shuttles in living systems. They catalyze a wide range of one- or two-electron redox reactions. Experimental investigations include UV-vis as well as infrared spectroscopy. FAD in aqueous solution exhibits a significantly shorter excited state lifetime than its analog, the flavin mononucleotide. This finding is explained by the presence of a "stacked" FAD conformation, in which isoalloxazine and adenine moieties form a  $\pi$ -complex. Stacking of the isoalloxazine and adenine rings should have an influence on the frequency of the vibrational modes. Density functional theory (DFT) studies of the closed form of FAD in microsolvation (explicit water) were used to reproduce the experimental infrared spectra, substantiating the prevalence of the stacked geometry of FAD in aqueous surroundings. It could be shown that the existence of the closed structure in FAD can be narrowed down to the presence of only a single water molecule between the third hydroxyl group (of the ribityl chain) and the N7 in the adenine ring of FAD.

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### **A reinvestigation of the deceptively simple reaction of toluene with OH, and the fate of the benzyl radical: a combined thermodynamic and kinetic study on the competition between OH-addition and H-abstraction reactions (Completo, 2020)**

SALTA, Z, KOSMAS, AM, MARC SEGOVIA, M. KIENINGER, VENTURA, O.N., BARONE, V

Theoretical Chemistry Accounts, v.: 139 p.:112 2020

Palabras clave: toluene hydroxyl radical photodegradation atmospheric chemistry density functional methods

Areas de conocimiento:

Ciencias Naturales y Exactas / Ciencias Químicas / Físico-Química, Ciencia de los Polímeros,

Electroquímica / Química computacional

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DOI: <https://doi.org/10.1007/s00214-020-02626-8>

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This work reports density functional and composite model chemistry calculations performed on the reactions of toluene with the hydroxyl radical. Both the experimentally observed H-abstraction

from the methyl group and possible OH-additions to the phenyl ring were investigated. Reaction enthalpies and barrier heights suggest that H-abstraction is more favorable than OH-addition to the ring. The calculated reaction rates at room temperature and the radical-intermediate product fractions support this view. At first sight, this might seem to disagree with the fact that, under most experimental conditions, cresols are observed in a larger concentration than benzaldehyde. Since the accepted mechanism for benzaldehyde formation involves H-abstraction, a contradiction arises that calls for a more elaborate explanation. In this first exploratory study, we provide evidence that support the preference of H-abstraction over OH-addition and present an alternative mechanism which shows that cresols can be actually produced also through H-abstraction and not only from OH-addition, thus justifying the larger proportion of cresols than benzaldehyde among the products.

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**Reinvestigation of the deceptively simple reaction of toluene with OH and the fate of the benzyl radical: The hidden routes to cresols and benzaldehyde (Completo, 2020)**

SALTA, Z., KOSMAS, AM., M. KIENINGER, MARC SEGOVIA, TASINATO, N., BARONE, V., VENTURA, O.N.

The Journal of Physical Chemistry A, v.: 124 28, p.:5917 - 5930, 2020

Palabras clave: radicals dft ccsd(t) heat of formation benzene derivatives atmospheric oxidation atmospheric chemistry

Areas de conocimiento:

Ciencias Naturales y Exactas / Ciencias Químicas / Físico-Química, Ciencia de los Polímeros, Electroquímica / Química computacional

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<https://pubs.acs.org/doi/full/10.1021/acs.jpca.0c03727>

In a previous work, we have investigated the initial steps of the reaction of toluene with the hydroxyl radical using several quantum chemical approaches including density functional and composite post-Hartree-Fock models. Comparison of H-abstraction from the methyl group and additions at different positions of the phenyl ring showed that the former reaction channel is favored at room temperature. This conclusion appears at first sight incompatible with the experimental observation of a lower abundance of the product obtained from abstraction (benzaldehyde) with respect to those originating from addition (cresols). Further reactions of the intermediate radicals with oxygen, water, and additional OH radicals are explored in this paper through theoretical calculations on more than 120 species on the corresponding potential energy surface. The study of the addition reactions, to obtain the cresols through hydroxy methylcyclohexadienyl intermediate radicals, showed that only in the case of o-cresol the reaction proceeds by addition of O<sub>2</sub> to the ring, internal H-transfer, and hydroperoxyl abstraction and not through direct H-abstraction. For both p- and m-cresol, instead, the reaction occurs through a higher-energy direct H-abstraction, thus explaining in part the observed larger concentration of the ortho isomer in the final products. It was also found that the benzyl radical, formed by H-abstraction from the methyl group, is able to react further if additional OH is present. Two reaction paths leading to o-cresol, two leading to p-cresol, and one leading to m-cresol were determined. Moreover, in this situation, the benzyl radical is predicted to produce benzyl alcohol, as was found in some experiments. The commonly accepted route to benzaldehyde was found to be not the energetically favored one. Instead, a route leading to the benzoyl radical (and ultimately to benzoic acid) with the participation of one water molecule was clearly more favorable, both thermodynamically and kinetically.

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**Enthalpies of formation of the benzyloxyl, benzylperoxyl, hydroxyphenyl radicals and related species on the potential energy surface for the reaction of toluene with the hydroxyl radical (Completo, 2019)** Trabajo relevante

VENTURA, O.N., M. KIENINGER, SALTA, Z., KOSMAS, A. M., BARONE, V.

Theoretical Chemistry Accounts, v.: 138 p.:115 2019

ISSN: 1432881X

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DOI: <https://doi.org/10.1007/s00214-019-2500-8>

<https://link.springer.com/journal/214>

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**Basis Set Effects in the Description of the Cl-O Bond in ClO and XCIO/ClOX Isomers (X= H, O, and Cl)**

### Using DFT and CCSD (T) Methods (Completo, 2019)

K. IRVING, M. KIENINGER, VENTURA, O.N.

Journal of Chemistry, v.: 2019 Article ID 4057848, 2019

Areas de conocimiento:

Ciencias Naturales y Exactas / Ciencias Químicas / Físico-Química, Ciencia de los Polímeros,

Electroquímica / Química Teórica y Computacional

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E-ISSN: 20909071

DOI: <https://doi.org/10.1155/2019/4057848>

<https://www.hindawi.com/journals/jchem/2019/4057848/abs/>

The performance of a group of density functional methods of progressive complexity for the description of the ClO bond in a series of chlorine oxides was investigated. The simplest ClO radical species and the two isomeric structures XClO/ClOX for each X=H, Cl, and O were studied using the PW91, TPSS, B3LYP, PBE0, M06, M06-2X, BMK, and B2PLYP functionals. Geometry optimizations and reaction enthalpies and enthalpies of formation for each species were calculated using Pople basis sets and the (aug)-cc-pVnZ Dunning sets, with n=D, T, Q, 5, and 6. For the calculation of enthalpies of formation, atomization and isodesmic reactions were employed. Both the precision of the methods with respect to the increase of the basis sets, as well as their accuracy, were gauged by comparing the results with the more accurate CCSD(T) calculations, performed using the same basis sets as for the DFT methods. The results obtained employing composite chemical methods (G4, CBS-QB3, and W1BD) were also used for the comparisons, as well as the experimental results when they are available. The results obtained show that error compensation is the key for successful description of molecular properties (geometries and energies) by carefully selecting the method and basis sets. In general, expansion of the one-electron basis set to the limit of completeness does not improve results at the DFT level, but just the opposite. The enthalpies of formation calculated at the CCSD(T)/aug-cc-pV6Z for the species considered are generally in agreement with experimental determinations and the most accurate theoretical values. Different sources of error in the calculations are discussed in detail.

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### Theoretical study of the reactions of the hydroselenyl radical (HSe $\cdot$ ) with the selenenic radical (HSeO $\cdot$ ) (Completo, 2018)

VEGA-TEIJIDO MA, M. KIENINGER, VENTURA, O.N.

Journal of Molecular Modeling, v.: 24 p.:3 2018

Palabras clave: selenium radicals sulfur radicals Alrichs M06

Areas de conocimiento:

Ciencias Naturales y Exactas / Ciencias Químicas / Físico-Química, Ciencia de los Polímeros,

Electroquímica / Química Teórica y Computacional

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<https://link.springer.com/article/10.1007/s00894-017-3535-1>

The formation of selenium species in some biological processes involves the generation of ionic and radical intermediates such as RSe $\cdot$ , RSe $\cdot$ , RSeO $\cdot$ , and RSeO $\cdot$ , among others. We performed a theoretical study of the possible mechanisms for the reaction of the two simplest Se radicals: the hydroselenyl (HSe $\cdot$ ) and selenenic (HSeO $\cdot$ ) radicals, in which the possible products, intermediates, and transition-state structures were investigated. Density functional theory (DFT) was applied at the B3LYP/6-311++G(3df,3pd) level and the Ahlrichs Coulomb fitting basis sets were employed with an effective core potential (ECP) for both Se atoms. The same procedure was used to calculate the electronic density. All calculations were also performed using the M06-2X functional, which describes weaker bonds better than B3LYP does. In the reaction of interest, the so-called CR complex (HSe $\cdots$ SeOH) is formed initially. After passing through the transition state TS1, cis-HSeSeOH is obtained as a product. If a low barrier is then overcome (passing through the transition state TS2), the trans-HSeSeOH species is obtained. The CR complex can also rearrange into the intermediate INT after overcoming the barrier presented by the transition state TS2. Additionally, the decomposition of INT to H<sub>2</sub>O and 1Se<sub>2</sub> is possible through another transition state. This reaction is not included in this study. We also observed a second possible route for the conversion of INT to one of the HSeSeOH species; this route occurs through two pathways (with transition states TS31 and TS32). A comparison of some of the results with those obtained for sulfur analogs along the same pathways is also presented in this work.

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### Using density functional theory to increase the accuracy of experimental crystal structures: The case of potassium peroxocarbonate (Completo, 2017)

FACCIO, R. , SAENZ MÉNDEZ, P. (SAENZ, P. EN ANTERIORES A 2007) , M. KIENINGER , VENTURA, O.N.

Journal of Molecular Structure, v.: 1146 p.:1 2017

Palabras clave: potassium peroxocarbonate density functional theory crystal structure optimization  
Areas de conocimiento:

Ciencias Naturales y Exactas / Ciencias Químicas / Físico-Química, Ciencia de los Polímeros, Electroquímica / Química Teórica y Computacional

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DOI: <https://doi.org/10.1016/j.molstruc.2017.05.115>

<https://www.sciencedirect.com/science/article/abs/pii/S002228601730724X>

A first principles simulation of the crystal structure of potassium peroxocarbonate is presented, using density functional methods (both local and semilocal) for the calculations. An experimental crystal structure with a seemingly inconsistent disposition of the peroxide bonds was used as initial input. Both geometry optimizations of the molecular structure and optimization of the cell size were performed. While cell parameters and heavier atom positions determined at the GGA level are very close to the experimental ones, there are important discrepancies in the positioning of the hydrogen atoms. As a result of these calculations, it was shown that the assignment of the peroxydic hydrogens and the peroxydic bond in the experimental structure was incorrect. A more accurate structure is presented and geometrical as well as cell parameters described. It is also shown that LDA is not accurate enough to describe this type of ionic crystals, because of overbinding of the ions, leading to incorrect cell parameters and volume. Our methodology was validated using DFT methods with several basis sets.

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**Atmospheric reactivity of HC equivalent to CCH<sub>2</sub>OH (2-propyn-1-ol) toward OH radicals: experimental determination and theoretical comparison with its alkyne analogue (Completo, 2015)**

GIBILISCO, RG , M. KIENINGER , VENTURA, O.N. , TERUEL, MA

RSC Advances, v.: 5 p.:10666 2015

Areas de conocimiento:

Ciencias Naturales y Exactas / Ciencias Químicas / Físico-Química, Ciencia de los Polímeros, Electroquímica / Química Teórica y Computacional

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DOI: [10.1039/C5RA19432F](https://doi.org/10.1039/C5RA19432F)

<https://pubs.rsc.org/en/content/articlelanding/2015/ra/c5ra19432f/unauth#!divAbstract>

The rate coefficient for the reaction of propargyl alcohol (2-propyn-1-ol, 2P1OL) with OH radicals has been determined using gas chromatography with a flame ionization detector (GC/FID) at 298 K and atmospheric pressure. The experimental value obtained by the relative method using methyl methacrylate and butyl acrylate as references was  $(2.05 \pm 0.30) \times 10^{11}$  cm<sup>3</sup> per molecule per s. The present value was compared with previous determinations and a theoretical study of the reaction was performed in order to explain the differences in reactivity of the alcohol with that of the corresponding alkyne (propyne, P). A full discussion of the addition and abstraction mechanisms was developed for 2P1OL at the density functional and ab initio composite model levels. It was found that addition is much faster than abstraction for propyne but occurs at approximately the same rate for 2P1OL. In this last case, however, abstraction of hydrogen from the C1 carbon leads to a complex which can react further to yield addition products. Thermodynamic and kinetic data calculated for these reactions suggest that the products would be the 1,2- and 1,3-propanediol radicals. These products would react further with O<sub>2</sub>, in the case where it is present in the reaction mixture.

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**Calculations of the infrared and Raman spectra of simple thiols and thiol-water complexes (Completo, 2011)**

M. KIENINGER , ON VENTURA

International Journal of Quantum Chemistry, v.: 111 7-8 , p.:1843 - 1857, 2011

Palabras clave: Química computacional tioles

Areas de conocimiento:

Ciencias Naturales y Exactas / Ciencias Químicas / Físico-Química, Ciencia de los Polímeros, Electroquímica / Química Teórica y Computacional

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DOI: [10.1002/qua.22890](https://doi.org/10.1002/qua.22890)

The frequencies and intensities of infrared and Raman spectra of H<sub>2</sub>S, CH<sub>3</sub>SH, CH<sub>3</sub>CH<sub>2</sub>SH, and CH<sub>2</sub>=CHCH<sub>2</sub>SH, isolated and complexed with one water molecule acting as a proton acceptor were calculated at the ab initio and density functional level. Hartree-Fock, MP2 and CCSD(T) methods were used both for the geometry optimization and spectra calculations at the molecular orbital level. The B3LYP, PBE0, and M06 exchange-correlation potentials were employed to calculate the same properties at the DFT level. Both Pople basis sets, 6-31+G(d) and 6-311++G(3df,2pd), and Dunning basis sets, aug-cc-pVTZ and aug-cc-pVQZ, were used. SH and CS frequency shifts upon water complexation were studied, and a discussion is performed on the expected relation between the CH and CS Raman activities, in view of their usefulness for studies in protein chemistry. Scaling factors for the vibrational frequencies were obtained for all the combination of methods and basis sets, and shown to be completely similar to the ones present in the literature when available. Scaling factors for the M06 method are presented for the first time with these basis sets. © 2010 Wiley Periodicals, Inc.

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#### **A Festschrift in Honour of Sándor Suhai's 65th Birthday (Completo, 2010)**

K. J. JALKANEN, M. KNAPP-MOHAMMADY, A. HOTZ-WAGENBLATT, K.-H. GLATTING, A. RETZMANN, M. KIENINGER, F. HERRMANN, Y. AOKI

Theoretical Chemistry Accounts, v.: 125 3-6, p.:101 - 105, 2010

Palabras clave: Química computacional bioquímica computacional

Áreas de conocimiento:

Ciencias Naturales y Exactas / Ciencias Químicas / Físico-Química, Ciencia de los Polímeros, Electroquímica / Química Teórica y Computacional

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This is a multidisciplinary multifocus issue of TCA titled the Suhai Festschrift Honorary Issue commemorating the 65th birthday of Professor Sándor Suhai and his many contributions to the fields of molecular biophysics, bioinformatics, theoretical chemistry, chemical physics and molecular biology. © Springer-Verlag 2009

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#### **On the structure, infrared and Raman spectra of the 2:1 cysteine-Zn complex (Completo, 2010)**

M. KIENINGER, ON VENTURA

Theoretical Chemistry Accounts, v.: 125 3-6, p.:279 - 291, 2010

Palabras clave: bioquímica computacional complejos de zinc tioles cisteína

Áreas de conocimiento:

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A recent study on the Raman spectrum of the cysteine zwitterion and anion, and the 2:1 (Cys)<sub>2</sub>Zn complex was reanalyzed employing B3LYP/6-311++G(3df,2pd) calculations in a simulated water environment. The spectra were rediscussed in light of the apparent incorrect structure determined in the original paper for this complex. The complex turns out to be tetrahedral and tetracoordinated instead of octahedral hexacoordinated, as initially proposed. The calculated Raman spectrum of the complex agrees very well with the experimental data, showing that both the geometrical and electronic structures are well represented. Three metal-ligand bands are found, two of them involving mostly the symmetrical and asymmetrical stretching of the Zn-N and Zn-S bonds. They were measured at 334 and 296 cm<sup>-1</sup> and calculated at 319 and 249 cm<sup>-1</sup>, respectively. The third band involves the stretching of Zn-S bonds but also skeletal vibrations of the ligand. This band, measured at 399 cm<sup>-1</sup> and calculated at 444 cm<sup>-1</sup>, has been previously assigned incorrectly to a Zn-O bond which does not actually exist since the CO<sub>2</sub>-1 fragments are located away from the Zn ion. © Springer-Verlag 2009

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#### **On the experimental structure of monoperoxocarbonic acid and the enthalpy of formation of carbonic acid, peroxyformic acid and monoperoxocarbonic acid in gas phase (Completo, 2009)**

M. KIENINGER, P. SAENZ, ON VENTURA

Chemical Physics Letters, v.: 480 1-3, p.:52 - 56, 2009

Palabras clave: Métodos de Funcionales de la Densidad Termoquímica Computacional Reacciones químicas Métodos Post-Hartree-Fock

Areas de conocimiento:

Ciencias Naturales y Exactas / Ciencias Químicas / Físico-Química, Ciencia de los Polímeros, Electroquímica / Química Teórica y Computacional

Medio de divulgación: Papel

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HCO<sub>3</sub><sup>-</sup> reacts with H<sub>2</sub>O<sub>2</sub> yielding monoperoxocarbonate (HCO<sub>4</sub><sup>-</sup>), an oxidizing agent able to epoxidize alkenes. The structures of HCO<sub>4</sub><sup>-</sup> and of parent monoperoxocarbonic acid (HPCA) are not known. However, the structure of the related peroxyformic acid (PFA) has been determined using microwave spectroscopy. We used in this work experimental and theoretical structures of PFA and formic acid, to suggest an approximate experimental structure for HPCA. Using a convenient set of isodesmic reactions, we also calculated the experimentally unknown enthalpies of formation of PFA, HPCA and carbonic acid. These values were further checked using model chemistry methods (G2(MP2), G3 and CBS-APNO).

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### **Comparison of large basis set DFT and MP2 calculations in the study of the barrier for internal rotation of 2,3,5,6-tetrafluoroanisole (Completo, 2007)**

M. KIENINGER, R. E. CACHAU, H. OBERHAMMER, ON VENTURA

International Journal of Quantum Chemistry, v.: 107 2, p.:403 - 417, 2007

Palabras clave: Métodos de Funcionales de la Densidad Métodos Post-Hartree-Fock Análisis conformacional

Areas de conocimiento:

Ciencias Naturales y Exactas / Ciencias Químicas / Físico-Química, Ciencia de los Polímeros, Electroquímica / Química Teórica y Computacional

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The barrier for internal rotation around the -OCH<sub>3</sub> bond in 2,3,5,6-tetrafluoroanisole was calculated using the density functional theory (DFT) and second order Moller-Plesset (MP2) methods with Pople basis sets up to 6-311++G(3rf,2p) and Jensen basis sets up to pc-3. The results are converged only if fairly large basis sets are used (at least 6-311 + +G(3df,2prf) or pc-2). Both the DFT and MP2 potential energy curves show internal structure. Two minima and three maxima are observed on the curves, arising from the interplay between lone-pair delocalization and changes in the hybridization around the oxygen atom, together with the attraction between the positively polarized hydrogens in the methyl group and the negatively polarized fluorine atom at the ortho position. These critical points are somehow ironed out by the addition of zero-point and thermal corrections to the energy curves. At this level, the MP2 method can describe reasonably well the previously determined single-well experimental rotational barrier,  $2.7 \pm 2.0$  kcal/mol at 298 K, while all DFT methods yield a much smaller result. As observed experimentally, the -OCH<sub>3</sub> group is perpendicular to the aryl ring in the equilibrium structure, although two very close minima with an intermediate hump at 90° are still observable. The theoretical free energy barrier of rotation at the MP2(full)/pc-2 level is  $2.0 \pm 1.0$  kcal/mol, in reasonable agreement with the experimental determination.

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### **Tautomeric forms of 2-thiobarbituric acid as studied in the solid, in polar solutions, and on gold nanoparticles (Completo, 2007)**

E. MÉNDEZ, M. F. CERDÁ, J. S. GANCHEFF, J. TORRES, M. KIENINGER, C. KREMER, J. CASTIGLIONI, ON VENTURA

The Journal of Physical Chemistry C, v.: 111 8, p.:3369 - 3383, 2007

Palabras clave: Métodos de Funcionales de la Densidad Reacciones químicas Isomerizaciones Nanopartículas Ácido tiobarbitúrico

Areas de conocimiento:

Ciencias Naturales y Exactas / Ciencias Químicas / Físico-Química, Ciencia de los Polímeros, Electroquímica / Química Teórica y Computacional

Medio de divulgación: Papel

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2-Thiobarbituric acid (TBA) coated gold nanoparticles (average diameter = 5.90 nm) were produced and studied by several experimental and theoretical methods. As part of this study, the molecular structure of TBA tautomers in the solid, in polar solutions, and adsorbed onto gold nanoparticles was studied. The resolution of this complicated system (10 possible isomers) was accomplished

with the aid of experimental (IR, UV-vis, and NMR) and theoretical (DFT and MP2) methods. The general conclusion is that there are two preeminent isomers, N1 and N10, with different stabilities in different media. N1, the keto-thione tautomer, is the most stable in gas phase ( $\Delta G^\circ_{298} \approx 8-9$  kcal/mol lower than the second-most stable isomer, depending on the method of calculation used). However, experimental spectroscopic data supported by the theoretical calculations strongly suggest an equilibrium between the tautomers N1 and N10 in methanol solution, where enolization of one keto group is produced by proton transfer from the methylene group, which is more acidic than the NH groups. With the use of the polarizable continuum method for simulating solvents, N10 is predicted to be even more stable than N1 by  $\Delta G^\circ_{298} \approx 1$  kcal/mol in methanol. On the other hand, the IR spectrum of the solid can be best explained by assuming that only N10 is present, a fact also supported by the observation that the IR spectrum of TBA absorbed onto gold nanoparticles can be explained by a larger ratio of [N10]/[N1] than that present in methanolic solution. Isomerization of  $N1 \rightleftharpoons N10$  can be explained by intervention of the solvent, proceeding faster in methanol solutions than in DMSO, where it is nevertheless observed after a time, according to the  $^{13}\text{C}$  NMR spectra. Our experiments support absorption of TBA onto gold nanoparticles through S-Au and N-Au interactions, with the preeminence of a N10-like enol structure. The experiments also demonstrate that the synthesized TBA-coated gold nanoparticles can autoassociate by hydrogen bonding to form larger structures. This same H-bonding capacity also assures that these coated nanoparticles act as thistles toward proteins in solution, binding them strongly, presumably not by chemical reaction but by a network of hydrogen bonds.

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**A new perspective in the lewis acid catalyzed ring opening of epoxides. Theoretical study of some complexes of methanol, acetic acid, dimethyl ether, diethyl ether, and ethylene oxide with boron trifluoride (Completo, 2006)**

P. SAENZ, M. KIENINGER, R. E. CACHAU, G. SEOANE, ON VENTURA

The Journal of Physical Chemistry A, v.: 110 41, p.:11734 - 11751, 2006

Palabras clave: Métodos de Funcionales de la Densidad Enlaces de hidrógeno Complejos moleculares

Areas de conocimiento:

Ciencias Naturales y Exactas / Ciencias Químicas / Físico-Química, Ciencia de los Polímeros, Electroquímica / Química Teórica y Computacional

Medio de divulgación: Papel

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Several 1:1, 1:2, and 2:2 complexes between  $\text{BF}_3$  and  $\text{CH}_3\text{OH}$  (Met),  $\text{CH}_3\text{COOH}$  (AcA),  $(\text{CH}_3)_2\text{O}$  (DME),  $(\text{CH}_3\text{CH}_2)_2\text{O}$  (DEE), and  $(\text{CH}_2)_2\text{O}$  (EOX) have been studied using ab initio (MP2) and density functional theory (DFT) (PBE, B3LYP) methods and the 6-311++G(3df,2pd) basis set. Geometrical structures and vibrational frequencies are reported, in most cases, for the first time. A detailed comparison of the vibrational frequencies for the  $\text{O}\cdots\text{BF}_3$  vibrational modes, as well as for the  $\nu(\text{OH})$  band in the methanol and acetic acid complexes with  $\text{BF}_3$ , is performed, and the theoretical frequency shifts are compared with the available experimental information. Thermochemical properties are calculated by employing counterpoise correction to alleviate the basis set superposition error. The DFT enthalpy of complexation of the 1:1 complexes results in the order of stability  $(\text{AcA})_2 > \text{AcA}:\text{BF}_3 > \text{DEE}:\text{BF}_3 > \text{DME}:\text{BF}_3 > \text{Met}:\text{BF}_3 > \text{EOX}:\text{BF}_3 > (\text{Met})_2$ ; in contrast, MP2 shows the noticeable difference that the  $\text{AcA}:\text{BF}_3$  complex is much less stable (similar to  $\text{Met}:\text{BF}_3$ ). The order of stability shows that, even though acetic acid prefers dimerization to complexation with  $\text{BF}_3$ , the case is exactly the opposite for methanol. In both cases, the interaction of  $\text{BF}_3$  with the dimer gives rise to very stable trimers. However, in contrast to the interaction of  $\text{BF}_3$  with the methanol dimer being stronger than that with the monomer, the interaction of  $\text{BF}_3$  with the acetic acid dimer is weaker than that with the monomer. The relative strength of the complexes, discussed in the context of  $\text{BF}_3$ -catalyzed ring opening of epoxides, suggests that the effect of the catalyst in a nonprotogenic solvent should be more properly ascribed to activation of the nucleophile instead of activation of the epoxide.

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**Molecular Structure and Internal Rotation in 2,3,5,6-Tetrafluoroanisole as Studied by Gas-Phase Electron Diffraction and Quantum Chemical Calculations (Completo, 2005)**

A. V. BELYAKOV, M. KIENINGER, R. E. CACHAU, ON VENTURA, H. OBERHAMMER

The Journal of Physical Chemistry A, v.: 109 2, p.:394 - 399, 2005

Palabras clave: Métodos de Funcionales de la Densidad Análisis conformacional

Areas de conocimiento:

Ciencias Naturales y Exactas / Ciencias Químicas / Físico-Química, Ciencia de los Polímeros, Electroquímica / Química Teórica y Computacional

Medio de divulgación: Papel

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The geometric structure of 2,3,5,6-tetrafluoroanisole and the potential function for internal rotation around the C(sp<sup>2</sup>)-O bond were determined by gas electron diffraction (GED) and quantum chemical calculations. Analysis of the GED intensities with a static model resulted in near-perpendicular orientation of the O-CH<sub>3</sub> bond relative to the benzene plane with a torsional angle around the C(sp<sup>2</sup>)-O bond of  $\tau(\text{C-O}) = 67(15)^\circ$ . With a dynamic model, a wide single-minimum potential for internal rotation around the C(sp<sup>2</sup>)-O bond with perpendicular orientation of the methoxy group [ $\tau(\text{C-O}) = 90^\circ$ ] and a barrier of  $2.7 \pm 1.6$  kcal/mol at planar orientation [ $\tau(\text{C-O}) = 0^\circ$ ] was derived. Calculated potential functions depend strongly on the computational method (HF, MP2, or B3LYP) and converge adequately only if large basis sets are used. The electronic energy curves show internal structure, with local minima appearing because of the interplay between electron delocalization, changes in the hybridization around the oxygen atom, and the attraction between the positively polarized hydrogen atoms in the methyl group and the fluorine atom at the ortho position. The internal structure of the electronic energy curves mostly disappears if zero-point energies and thermal corrections are added. The calculated free energy barrier at 298 K is  $2.0 \pm 1.0$  kcal/mol, in good agreement with the experimental determination.

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**A comparative density functional study of the torsional potential of 4-fluoro (trifluoromethoxy)benzene and related species (Completo, 2004)**

M. KIENINGER, ON VENTURA, G. H. F. DIERCKSEN

Chemical Physics Letters, v.: 389 4-6, p.:405 - 412, 2004

Palabras clave: Métodos de Funcionales de la Densidad Análisis conformacional

Areas de conocimiento:

Ciencias Naturales y Exactas / Ciencias Químicas / Físico-Química, Ciencia de los Polímeros,

Electroquímica / Química Teórica y Computacional

Medio de divulgación: Papel

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B3LYP density functional methods with conventional and especially derived basis sets are applied to determine the torsional potential around the aryl-O bond in 4-fluoro (trifluoromethoxy)benzene (1), trifluoromethoxybenzene (2), 4-fluoro anisole (3) and anisole (4). It is found that both 1 and 2 exhibit a minimum at the perpendicular-planes [o]-form conformation, opposite to 3 and 4, which present minima at the eclipsed [e]-form conformation. A very flat secondary minimum for the [e]-form is found for both 1 and 2 with the larger basis sets, but it is unable to sustain any vibrational level. The precision and accuracy of the B3LYP calculations are determined through the study of methyl vinyl ether and trifluoromethyl vinyl ether at the MP2 and QCISD levels

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**Density functional computational thermochemistry: Determination of the enthalpy of formation of methanethial-S,S-dioxide (sulfene) (Completo, 2003)**

ON VENTURA, M. KIENINGER, P. A. DENIS

The Journal of Physical Chemistry A, v.: 107 4, p.:518 - 521, 2003

Palabras clave: Métodos de Funcionales de la Densidad Termoquímica Computacional Métodos

Post-Hartree-Fock

Areas de conocimiento:

Ciencias Naturales y Exactas / Ciencias Químicas / Físico-Química, Ciencia de los Polímeros,

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The enthalpy of formation of methanethial-S,S-dioxide (CH<sub>2</sub>SO<sub>2</sub>) has been determined by the use of isodesmic and nonisodesmic reactions, with individual enthalpies calculated by employing density functional methods and the CBS-QB3 model chemistry. After assessing the possible errors in the methodology, it was concluded that this value can be expressed as  $\Delta_f H^\circ_{298}(\text{CH}_2\text{SO}_2) = -144.7 \pm 8.4$  kJ/mol.

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**Erratum: Complete basis set and density functional determination of the enthalpy of formation of the controversial HO<sub>3</sub> radical. A discrepancy between theory and experiment (Chemical Physics Letters (2002) 365 (440-449) PII S000926140201432X) (Completo, 2003)**

P. A. DENIS, M. KIENINGER, ON VENTURA, G. H. F. DIERCKSEN

Chemical Physics Letters, v.: 377 3-4, p.:483 - 484, 2003

Areas de conocimiento:

Ciencias Naturales y Exactas / Ciencias Químicas / Físico-Química, Ciencia de los Polímeros, Electroquímica / Química Teórica y Computacional

Medio de divulgación: Papel

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**Density functional computational thermochemistry: Solving the discrepancy between MO and DFT calculations on the enthalpy of formation of sulfine, CH<sub>2</sub>=S=O (Completo, 2002)**

ON VENTURA, M. KIENINGER, P. A. DENIS, R. E. CACHAU

Chemical Physics Letters, v.: 355 3-4, p.:207 - 213, 2002

Palabras clave: Métodos de Funcionales de la Densidad Termoquímica Computacional Métodos Post-Hartree-Fock Sulfine

Areas de conocimiento:

Ciencias Naturales y Exactas / Ciencias Químicas / Físico-Química, Ciencia de los Polímeros, Electroquímica / Química Teórica y Computacional

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The enthalpy of formation of sulfine is computed at the density functional (DFT) level to solve the discrepancy between previously recommended theoretical values. In agreement with the most recent CBS-QB3 calculations, which predict a value of  $-30 \pm 6$  kJ/mol, DFT calculations on isodesmic reactions predict a value of  $-38 \pm 10$  kJ/mol. Previous estimations of  $-9 \pm 14$  kJ/mol (at the MO level) and  $-52 \pm 10$  kJ/mol (at the DFT level) are discussed and shown to be artifacts of the methods of calculation employed.

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**Computational determination of the enthalpy of formation of alkylthial S-oxides and alkylthione S-oxides: A study of (Z)-propanethial-S-oxide, the lachrymatory factor of the onion (Allium cepa) (Completo, 2002)**

M. KIENINGER, ON VENTURA

Physical Chemistry Chemical Physics, v.: 4 18, p.:4328 - 4333, 2002

Palabras clave: Métodos de Funcionales de la Densidad Termoquímica Computacional Métodos Post-Hartree-Fock

Areas de conocimiento:

Ciencias Naturales y Exactas / Ciencias Químicas / Físico-Química, Ciencia de los Polímeros, Electroquímica / Química Teórica y Computacional

Medio de divulgación: Papel

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A general computation procedure for the determination of unknown enthalpies of formation of alkylthial or alkylthione S-oxides, based on the recent accurate determination of the enthalpy of formation of methanethial S-oxide, is proposed. The method relies on the use of isodesmic reactions involving the sulfoxide and sulfide of the species of interest, with the individual energies calculated at the CBS-QB3 level. A discussion is given about the convenience of using density functional theory (DFT) instead of the CBS-QB3 model chemistry, especially for large compounds. To exemplify the method, the enthalpies of formation of ethanethial-S-oxide ( $-74.7 \pm 8.4$  kJ mol<sup>-1</sup>), propanethione-S-oxide ( $-112.1 \pm 8.4$  kJ mol<sup>-1</sup>) and propanethial-S-oxide ( $-94.1 \pm 8.4$  kJ mol<sup>-1</sup>) are calculated, as well as those of the necessary sulfides propanethial ( $50.4 \pm 8.4$  kJ mol<sup>-1</sup>) and propanethione ( $28.0 \pm 8.4$  kJ mol<sup>-1</sup>). These values were derived on the basis of an independent theoretical estimation of the enthalpy of formation of thioformaldehyde ( $113.2 \pm 4.2$  kJ mol<sup>-1</sup>, in agreement with the experimental value,  $118 \pm 8.4$  kJ mol<sup>-1</sup>). The use of the same method for evaluating the enthalpy of formation of ethanethial however, gave  $68.1 \pm 4.2$  kJ mol<sup>-1</sup>, higher than the experimental value,  $50 \pm 8$  kJ mol<sup>-1</sup>. Convincing evidence is given that the theoretical estimation should be preferred to the experimental one in this case. Moreover, it was determined that the most stable isomer of propanethial S-oxide is in fact the Z-conformer, where the terminal methyl group is about 120° out of the plane of the C=S=O group. However, the C=S and =CH-CH<sub>2</sub>-bond lengths are very different from the recent experimental determination. A comparison with the experimental and theoretical results for the lower members of the series suggests that the model assumed for deriving the bond lengths from the microwave spectrum may be at fault. The whole process is validated by comparison of the enthalpies of formation of thioaldehydes and thioketones to the known enthalpies of formation of aldehydes and ketones.

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**Complete basis set and density functional determination of the enthalpy of formation of the**

### **controversial HO3 radical: A discrepancy between theory and experiment (Completo, 2002)**

P. A. DENIS, M. KIENINGER, ON VENTURA, R. E. CACHAU, G. H. F. DIERCKSEN

Chemical Physics Letters, v.: 365 5-6, p.:440 - 449, 2002

Palabras clave: Métodos de Funcionales de la Densidad Termoquímica Computacional Métodos Post-Hartree-Fock Química atmosférica

Areas de conocimiento:

Ciencias Naturales y Exactas / Ciencias Químicas / Físico-Química, Ciencia de los Polímeros, Electroquímica / Química Teórica y Computacional

Medio de divulgación: Papel

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Enthalpies of formation of the HOOOH molecule and HOOO radical were determined accurately employing density functional (DFT), coupled-clusters (CC) and complete basis set (CBS) extrapolation methods. The enthalpy of formation of the HO3 radical was determined as  $7.1 \pm 2$  kcal/mol at 298 K through a series of calculations employing the isodesmic reaction  $\text{HOOOH} + \text{OH} \rightarrow \text{HOH} + \text{HOOO}$ . This value is in disagreement with the experimental one of Speranza,  $-1 \pm 5$  kcal/mol. The enthalpy of formation of HOOOH, calculated at the extrapolated CBS/CCSD(T) and CBS-APNO levels, amounts to  $-21.1 \pm 1$  kcal/mol, also in disagreement with the experimentally determined upper limit of  $-26.0$  kcal/mol. Further examination of the procedure used to determine this value from the raw experimental data, suggests that this value is not as reliable as originally thought (by Speranza). The data should be reexamined and perhaps supplemented with additional experiments.

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### **Density functional computational thermochemistry: Isomerization of sulfine and its enthalpy of formation (Completo, 2001)**

ON VENTURA, M. KIENINGER, P. A. DENIS, R. E. CACHAU

The Journal of Physical Chemistry A, v.: 105 43, p.:9912 - 9916, 2001

Palabras clave: Métodos de Funcionales de la Densidad Termoquímica Computacional Reacciones químicas Métodos Post-Hartree-Fock

Areas de conocimiento:

Ciencias Naturales y Exactas / Ciencias Químicas / Físico-Química, Ciencia de los Polímeros, Electroquímica / Química Teórica y Computacional

Medio de divulgación: Papel

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Density functional (DFT), second-order perturbation theory (MP2), and coupled-cluster [(CCSD(T))] calculations using Pople basis sets up to 6-311 ++G(3df,2pd) and Dunning correlation consistent basis sets have been employed to determine the enthalpy of formation of sulfine,  $\text{CH}_2\text{SO}$ , **1**, using the isodesmic reaction  $\text{CH}_2\text{S} + \text{SO}_2 \rightleftharpoons \text{CH}_2\text{SO} + \text{SO}$ . Previous calculations showed an inconsistency between the enthalpy of formation obtained using this methodology,  $\Delta_f H^\circ_{298.15(1)} = -52 \pm 10$  kJ/mol, and the value obtained employing the isomerization reaction  $\text{CH}_2\text{SO} (1) \rightleftharpoons \text{HC}(=\text{O})\text{SH} (2)$  if Benson estimate for the enthalpy of formation of isomer **2** (thioformic acid) was employed. This result was particularly vexing, since the computed enthalpy of formation of **1** was reasonably in agreement with Benson own estimate. In this paper we extended our previous study using the reactions  $\text{HC}(=\text{O})\text{-XH} + \text{RH} \rightleftharpoons \text{H}_2\text{CO} + \text{R-XH}$  with R = H, Me, Et, Pr, and i-Pr. X was either sulfur, to obtain the enthalpy of formation of **2**, or oxygen, to assess the errors to be expected in the use of these reactions for the evaluation of  $\Delta_f H^\circ$ . The result,  $\Delta_f H^\circ_{298.15(2)} = -121 \pm 8$  kJ/mol, arrived at after a critical assessment of B3LYP, MP2, and CCSD(T) results, is in complete agreement with the value of  $-126 \pm 4$  kJ/mol estimated by Benson. This implies that the isomerization reaction cannot be employed for the determination of the enthalpy of formation of sulfine. We ascribe this inadequacy to the errors introduced due to the change in the oxidation state of sulfur.

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### **Density functional computational thermochemistry: Determination of the enthalpy of formation of sulfine, $\text{CH}_2=\text{S}=\text{O}$ , at room temperature (Completo, 2000)**

ON VENTURA, M. KIENINGER, R. E. CACHAU, S. SUHAI

Chemical Physics Letters, v.: 329 1-2, p.:145 - 153, 2000

Palabras clave: Métodos de Funcionales de la Densidad Termoquímica Computacional Métodos Post-Hartree-Fock

Areas de conocimiento:

Ciencias Naturales y Exactas / Ciencias Químicas / Físico-Química, Ciencia de los Polímeros, Electroquímica / Química Teórica y Computacional

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Density functional and coupled-cluster calculations using Pople basis sets up to 6-311++G(3df,2pd) have been employed to determine the heat of formation of sulfine, CH<sub>2</sub>SO, 1, using the isodesmic reaction CH<sub>2</sub>S+SO<sub>2</sub>⇌CH<sub>2</sub>SO+SO. Other reactions, employed previously to determine the enthalpy of formation of sulfine at the CAS-SDCI/ CASSCF ab initio level, were used as well. The analysis of the results shows that: (a) the errors in the calculation of the enthalpies for the individual molecules do cancel reasonably only for the isodesmic reaction, and not for those used previously; (b) density functional methods produce smaller errors than CCSDT in the calculation of the enthalpies of formation of the molecules involved in this reaction; (c) the actual heat of formation of sulfine is determined as  $\Delta_f H_o 298.15(1) = -52 \pm 10$  kJ/mol, more in agreement with the prediction of Benson than with the ab initio value derived by Ruttink et al.; (d) the proton affinity of sulfine, calculated at the density functional level (792.0 kJ/mol) agrees reasonably well with the experimental result, 787.6±2.6 kJ/mol, but the enthalpy of formation of 1 derived from this proton affinity using the assumptions of Ruttink or Bouchoux is in disagreement with the value determined previously.

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**Density functional theory is more accurate than coupled-cluster theory in the study of the thermochemistry of species containing the F-O bond (Completo, 1999)** Trabajo relevante

ON VENTURA, M. KIENINGER, R. E. CACHAU

The Journal of Physical Chemistry, v.: 103 1, p.:147 - 151, 1999

Palabras clave: Métodos de Funcionales de la Densidad Termoquímica Computacional Óxidos de flúor Métodos Post-Hartree-Fock

Areas de conocimiento:

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The standard singles and doubles coupled-cluster method including perturbational treatment of connected triple excitations, CCSD(T), and density functional methods, DFT, using a large, uncontracted, atomic natural orbital (ANO) basis set were employed for calculating the enthalpies of formation of some first-row atoms (H, N, O, F) as well as diatomic and triatomic molecules formed with them. Molecular enthalpies of formation at 298.15 K were obtained from enthalpies of reaction of the atoms, homonuclear diatomic molecules, and isodesmic reactions. It is shown that the errors are the minimum when isodesmic reactions are used. However, contrary to accepted belief, CCSD(T) gives a larger deviation from experiment than DFT in the latter case. DFT exhibits similar accuracy when using a very small basis set (6-31G\*) to that with the extended basis set, while the errors obtained with CCSD(T) are much larger. It is concluded that DFT is a more accurate and convenient computational tool than CCSD(T) for the thermochemical study of species containing the F-O bond.

**Density functional and coupled-cluster calculations of isodesmic reactions involving fluorine oxides (Completo, 1999)**

ON VENTURA, R. E. CACHAU, M. KIENINGER

Chemical Physics Letters, v.: 301 3-4, p.:331 - 335, 1999

Palabras clave: Radicales Métodos de Funcionales de la Densidad Óxidos de flúor

Areas de conocimiento:

Ciencias Naturales y Exactas / Ciencias Químicas / Físico-Química, Ciencia de los Polímeros, Electroquímica / Química Teórica y Computacional

Medio de divulgación: Papel

ISSN: 00092614

Some isodesmic reactions, involving the fluorine oxide radical FO, have been studied employing density functional theory (DFT) and coupled-cluster (CC) calculations with an extended, uncontracted basis set. It is shown that CCSD(T) calculations can give more accurate enthalpies of reaction than DFT in some of the non-isodesmic reactions. DFT, however, gives more accurate results than CCSD(T) for the isodesmic reactions considered.

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**Synthesis, characterization, and crystal structure of [ReO(Me<sub>4</sub>tu)<sub>4</sub>](PF<sub>6</sub>)<sub>3</sub> (tu = thiourea) (Completo, 1999)**

D. GAMBINO, E. KREMER, E. J. BARAN, A. MOMBRÚ, L. SUESCUN, R. MARIEZCURRENA, M. KIENINGER, ON VENTURA

Zeitschrift für anorganische und allgemeine Chemie, v.: 625 5 , p.:813 - 819, 1999

Palabras clave: Métodos de Funcionales de la Densidad Complejos de Metales de Transición urea  
Areas de conocimiento:

Ciencias Naturales y Exactas / Ciencias Químicas / Físico-Química, Ciencia de los Polímeros,  
Electroquímica / Química Teórica y Computacional

Medio de divulgación: Papel

ISSN: 00442313

E-ISSN: 15213749

A new Rev oxo complex with tetramethylthiourea,  $[\text{ReO}(\text{Me}_4\text{tu})_4](\text{PF}_6)_3$ , has been synthesized by reduction of perrhenate with tin(II) chloride in strongly acidic solution in the presence of excess tetramethylthiourea. The complex has been characterized by elemental analysis and electronic and FTIR spectroscopy. The molecular structure of the compound was determined by X-ray diffraction methods. The coordination polyhedron is a regular square pyramid with the substituted thiourea sulfur atoms in the equatorial positions [ $d(\text{Re}-\text{S}) = 2.339(3) \text{ \AA}$ ] and the oxo ligand located in the summit [ $d(\text{Re}-\text{O}) = 1.63(2) \text{ \AA}$ ]. Computational methods were employed to analyze the geometric and electronic structures of tetramethylthiourea and thiourea. Quantum mechanical studies suggest steric hindrance as the reason for the stabilization of the  $\text{ReO}_3^+$  center instead of the  $\text{ReII}$  one.

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### **Computational chemistry as an analytical tool: Thermochemical examples in atmospheric chemistry (Completo, 1998)**

ON VENTURA, M. KIENINGER

Pure and Applied Chemistry, v.: 70 12, p.:2301 - 2307, 1998

Palabras clave: Radicales Termoquímica Computacional Teoría de funcionales de la densidad  
Química atmosférica

Areas de conocimiento:

Ciencias Naturales y Exactas / Ciencias Químicas / Físico-Química, Ciencia de los Polímeros,  
Electroquímica / Química Teórica y Computacional

Medio de divulgación: Papel

ISSN: 00334545

E-ISSN: 13653075

Computational chemistry is one area of research which has evolved to the point in which it can be used profitably in cooperation with experimental, traditional chemistry. The ever increasing power of modern computers coupled with the development of new theoretical approaches can be used for accurate and precise prediction of molecular properties. One of the most useful applications of computational chemistry is the prediction of properties difficult or impossible to measure experimentally. In some cases, computational chemistry can be used to predict certain properties with accuracy that rivals or even excels that of the best experiments available. Thus, nowadays, the computer can be looked at as another analytical instrument, which can be used like a spectrometer, for instance, to search for solutions to difficult chemical problems. In this paper we introduce in a simplified manner the way in which computational chemistry can be used for that purpose. Some examples are given, taken from our own work on the stratospheric chemistry of substances that may destroy the ozone layer.

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### **Density functional and ab initio study of the free radical MgNC (Completo, 1998)**

M. KIENINGER, K. IRVING, F. RIVAS-SILVA, A. PALMA, ON VENTURA

Journal of Molecular Structure THEOCHEM, v.: 422 1-3, p.:133 - 141, 1998

Palabras clave: Radicales Métodos de Funcionales de la Densidad MgCN Espectroscopía

Areas de conocimiento:

Ciencias Naturales y Exactas / Ciencias Químicas / Físico-Química, Ciencia de los Polímeros,  
Electroquímica / Química Teórica y Computacional

Medio de divulgación: Papel

ISSN: 01661280

A new "non-terrestrial" molecule present in the envelope of the carbon star IRC + 10216 was described for the first time in 1986. Recently, this molecule was identified as the free radical MgNC, the first Mg-containing molecule in space. We present here the first density functional study performed on this radical, as well as on its isomer MgCN and the transition state connecting these species. It is shown that the optimum geometry obtained at the Becke3LYP/6-311+G(3df) level leads to the most exact rotational constants  $B_e$  and  $B_0$  calculated up to now. It is also shown that the energy differences between the three species are completely in agreement with the best ab initio calculations available. Furthermore, it is shown that the popular MP2 method fails for this system in the same way that has been demonstrated for other radicals.

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### **A discrepancy between experimental and theoretical thermochemical characterization of some oxygen fluorides (Completo, 1998)**

M. KIENINGER, M. SEGOVIA, ON VENTURA

Chemical Physics Letters, v.: 287 5-6, p.:597 - 600, 1998

Palabras clave: Métodos de Funcionales de la Densidad Termoquímica Computacional Óxidos de flúor

Areas de conocimiento:

Ciencias Naturales y Exactas / Ciencias Químicas / Físico-Química, Ciencia de los Polímeros, Electroquímica / Química Teórica y Computacional

Medio de divulgación: Papel

ISSN: 00092614

The recently recommended NIST-JANAF Thermochemical Table values for the thermochemical properties of oxygen fluorides are examined critically on the basis of high-level density functional and ab initio G2 calculations. Special attention is given to the enthalpies of formation and it is concluded that, although the proposed values for OF(g), FOO(g) and FOF(g) are reasonable and in agreement with our previously recommended values, the enthalpy of formation recommended for FOOF is too low. A value about 50% larger is proposed and it is recommended that the original 1959 experimental determination of this enthalpy of formation be repeated.

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### **Glycine conformations: Gradient-corrected DFT-studies (Completo, 1998)**

M. KIENINGER, S. SUHAI, ON VENTURA

Journal of Molecular Structure THEOCHEM, v.: 433 1-3, p.:193 - 201, 1998

Palabras clave: Métodos de Funcionales de la Densidad Análisis conformacional Glicina Aminoácidos

Areas de conocimiento:

Ciencias Naturales y Exactas / Ciencias Químicas / Físico-Química, Ciencia de los Polímeros, Electroquímica / Química Teórica y Computacional

Medio de divulgación: Papel

ISSN: 01661280

Different exchange-correlation potential combinations have been applied for the two lowest lying glycine conformations. The energy difference of - 1.1 kcal mol<sup>-1</sup> obtained with the Becke3 exchange-Vosko, Wilk, Nusair correlation potential compares reasonably with the experimental value of - 1.4 ± 0.4 kcal mol<sup>-1</sup>. The geometrical structure obtained is in good agreement with MP2 results and experiment. It seems that the gradient-correction in the correlation functional may not be important for describing the conformers of glycine.

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### **Density functional investigations of carboxyl free radicals: Formyloxyl, acetyloxyl, and benzoyloxyl radicals (Completo, 1998)**

M. KIENINGER, ON VENTURA, S. SUHAI

International Journal of Quantum Chemistry, v.: 70 2, p.:253 - 267, 1998

Palabras clave: Radicales Teoría de funcionales de la densidad Reacciones químicas

Areas de conocimiento:

Ciencias Naturales y Exactas / Ciencias Químicas / Físico-Química, Ciencia de los Polímeros, Electroquímica / Química Teórica y Computacional

Medio de divulgación: Papel

ISSN: 00207608

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The structure of the lowest electronic states of HCOO in C<sub>2v</sub> and C<sub>s</sub> symmetries were optimized employing density functional theory (DFT) methods with extended basis sets including up to f- (on C and O) and d- (on H) polarization functions. Generalized gradient functionals (BLYP) and adiabatically connected functionals (B3LYP and B3PW91) were employed for studying HCOO<sup>-</sup>, as well as the isomer HOCÓ (trans), the dissociation limit H+ CO<sub>2</sub>, and the transition state for the decomposition. At the best DFT levels employed, the ground state of HCOO is 2A<sub>1</sub> (in C<sub>2v</sub>) with equal C - O bond lengths, while the low-lying 2B<sub>2</sub> state is only about 4 kJ/mol above (without inclusion of zero-point energies). The broken-symmetry 2A' state (with unequal C - O bond lengths, i.e., C<sub>s</sub> symmetry) is predicted to be about 13 kJ/mol above the 2A<sub>1</sub> state and to be a transition state for the isomerization HCOO (2A<sub>1</sub>) → HOCÓ (2A') with the trans-HOCO isomer about 55 kJ/mol more stable. These facts agree closely with the most recent CASPT2/ANO calculations on this system. Therefore, it is concluded that some DFT models can be used safely for the study of larger radicals of the same type (despite several drawbacks discussed at length in this study).

B3PW91, using several basis sets, is subsequently applied to the study of the possible reaction mechanisms of acetyloxyl radical, which exhibits a much more complicated path than formyloxyl, due to the presence of the methyl group. The optimum structures of isomers with coplanar or perpendicular CH and CO bonds were obtained for CH<sub>3</sub>COO and two saddle points identified on the path of decomposition into CH<sub>3</sub> and CO<sub>2</sub>. On the other side, saddle points for isomerization into CH<sub>3</sub>OCO and CH<sub>2</sub>COOH were also located, and the decomposition of the former to CH<sub>3</sub>O+CO investigated. Finally, the structure of the benzoyloxyl radical (C<sub>6</sub>H<sub>5</sub>COO) and its possible decomposition products were investigated along the same lines

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### **An analysis of dipole polarizabilities using density functional theory: N<sub>2</sub>, H<sub>2</sub>, F- and HF (Completo, 1997)**

M. KIENINGER, ON VENTURA, I. CERNUÁK

Journal of Molecular Structure, v.: 436 p.:489 - 501, 1997

Palabras clave: Métodos de Funcionales de la Densidad Polarizabilidades

Areas de conocimiento:

Ciencias Naturales y Exactas / Ciencias Químicas / Físico-Química, Ciencia de los Polímeros, Electroquímica / Química Teórica y Computacional

Medio de divulgación: Papel

E-ISSN: 00222860

An analysis of static dipole polarizability of one atomic anion (F<sup>-</sup>) and three diatomic molecules (H<sub>2</sub>, N<sub>2</sub> and HF) has been performed at the density functional theory (DFT) level. Dunning correlation-consistent basis sets, ranging from the smallest cc-pVDZ to the aug-cc-pV5Z were employed systematically for all the molecules. Additionally, special types of basis sets, derived specifically for the calculation of polarizabilities in an ab initio environment, were employed in some cases. Calculations of the polarizabilities were performed at the DFT level employing the BLYP, B3LYP and B3PW91 exchange-correlation potentials, and the accuracy of the results was judged against experimental data on the one hand, and the polarizabilities calculated at the Hartree-Fock (HF), MP2, MP4(SDTQ), QCISD and CCSD levels on the other. In all the cases studied, it was observed that the quality of the results followed the order (from worst to best) HF < MP2 < BLYP < B3LYP < B3PW91 ≈ MP4~QCISD~CCSD, demonstrating that DFT (B3PW91 in particular) is a convergent alternative to highly correlated post-Hartree-Fock methods. A full discussion of basis-set effects is performed.

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### **Equilibrium structure of the carbon dioxide water complex in the gas phase: An ab initio and density functional study (Completo, 1997)**

M. KIENINGER, ON VENTURA

Journal of Molecular Structure THEOCHEM, v.: 390 1-3, p.:157 - 167, 1997

Palabras clave: Métodos de Funcionales de la Densidad Enlaces de hidrógeno

Areas de conocimiento:

Ciencias Naturales y Exactas / Ciencias Químicas / Físico-Química, Ciencia de los Polímeros, Electroquímica / Química Teórica y Computacional

Medio de divulgación: Papel

ISSN: 01661280

High-level ab initio (MP2/6-311++G(2d,2p) geometry, Gaussian-2, MP4(SDTQ) and QCISD(T) binding energies) and density-functional (Becke3LYP/6-311++G(2df,2pd)) calculations have been performed on the charge-transfer complex between water and carbon dioxide. The complex appears to have two equivalent non-planar minima of C<sub>s</sub> symmetry. Minima are separated by transition states with C<sub>1</sub> symmetry, whereas the totally planar structure with C<sub>2v</sub> symmetry is a second-order transition state. All the critical points lie at approximately the same energy (less than 0.05 kJ mol<sup>-1</sup> difference). Therefore, the experimentally observable structure should be planar. The best equilibrium intermolecular distance for this complex calculated at the MP2/6-311++G(2d,2p) level is 2.800 Å. Our best estimate of the observable intermolecular distance (corrected for anharmonicity) is 2.84 Å, in agreement with the experimentally derived value of 2.836 Å. Our best estimate of the binding energy at the QCISD(T) level, taking into account the variation of the distance owing to anharmonicity and the use of more sophisticated theoretical treatments, is -12.0 ± 0.2 kJ mol<sup>-1</sup>. Our best estimate of the barrier to internal rotation, also at the MP2/6-311++G(2d,2p) level, is 4.0 kJ mol<sup>-1</sup>, outside the error limits of the experimental determination (3.64 ± 0.04 kJ mol<sup>-1</sup>). Density functional theory at the level employed here gives an equilibrium intermolecular distance that is too large (2.857 Å), a binding energy that is too small (8.1 kJ mol<sup>-1</sup>), attributable neither to geometry nor to the basis set, and also a barrier to internal rotation that is slightly too small (3.39 kJ mol<sup>-1</sup>). The overall picture is, however, reasonably good.

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### **The Water Dimer: Post-Hartree-Fock and Density Functional Calculations on the Potential Energy Surface (Completo, 1997)**

ON VENTURA, M. KIENINGER, S. SUHAI, G. H. F. DIERCKSEN

Molecular Engineering, v.: 7 3-4, p.:317 - 348, 1997

Palabras clave: Métodos de Funcionales de la Densidad Enlaces de hidrógeno Dímero de agua

Areas de conocimiento:

Ciencias Naturales y Exactas / Ciencias Químicas / Físico-Química, Ciencia de los Polímeros,

Electroquímica / Química Teórica y Computacional

Medio de divulgación: Papel

ISSN: 09255125

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Conventional ab initio and density functional methods with extended basis sets were employed in the study of a path on the water-dimer potential energy surface. The results show that density functional methods do depend strongly on the type of exchange-correlation potential employed, as well as on the quality of the basis sets similarly to conventional ab initio methods and on the density of the grid. Gradient-corrected methods behave, as expected, better than uncorrected ones, the BeckeLeeYangParr (BLYP) potential being the one that gives the best results. However, too large chemical- and hydrogen-bond lengths and absolute energies, as well as too small relative total and correlation energies demonstrate that even BLYP calculations with a relative large basis set are not good as MP2 calculations of the same size. Adiabatically connected functionals (ACM), represented in this work by B3PW91, provide an improvement on the whole surface.

### **Density functional study of isomerization of fluoro- and chloroformaldehyde radical cations (Completo, 1996)**

ON VENTURA, M. KIENINGER, E. L. COITIÑO

Journal of Computational Chemistry, v.: 17 11, p.:1309 - 1317, 1996

Palabras clave: Radicales Métodos de Funcionales de la Densidad Reacciones químicas

Isomerizaciones haloformaldehído

Areas de conocimiento:

Ciencias Naturales y Exactas / Ciencias Químicas / Físico-Química, Ciencia de los Polímeros,

Electroquímica / Química Teórica y Computacional

Medio de divulgación: Papel

ISSN: 01928651

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Ab initio and density functional (DFT) calculations were performed on radical cations with the formula  $\text{HXCO}^+$  ( $X = \text{H, F, and Cl}$ ) and their isomers  $\text{XCOH}^+$ . Hartree-Fock, Møller-Plesset at second order (MP2), and quadratic configuration interaction including singles and doubles (QCISD) methods were employed for geometry optimizations at the ab initio level. Becke 1988 and three-parameter exchange potentials, together with Vosko-Wilk-Nusair (VWN) and Lee-Yang-Parr (LYP) correlation potentials (BVWN, BLYP, and B3LYP) were used for the DFT calculations. HF and MPn isomerization energies are severely in error, mostly due to a bad description of the  $\text{XHCO}^+$  cation radicals at the Hartree-Fock level, leading to oscillatory behavior of the perturbation series. QCISD methods, at least, are needed to obtain accurate results at the conventional ab initio level, even using large extended basis sets. B3LYP results are most similar to QCISD results for the isomerization energies of the three cation radicals. Parent neutral species are also described to a high degree of accuracy. B3LYP methods are faster than QCISD (and as exact as them) for all the cases studied here. MP2 methods, although giving incorrect results, are faster than B3LYP up to about 80 basis functions. For larger problems, B3LYP methods are faster. The best theoretical results obtained indicate that fluoro- and chloroformaldehyde cation radicals are less stable than their hydroxyfluoro- and hydroxychloromethylene isomers, the reverse situation than for the formaldehyde cation radical. The best values found in this article for the isomerization energy of  $\text{XHCO}^+$  are  $-26 \pm 2$  kJ/mol ( $X = \text{H}$ ),  $+37 \pm 2$  kJ/mol ( $X = \text{F}$ ), and  $+28 \pm 2$  kJ/mol ( $X = \text{Cl}$ ). Ionization energies of 10.9, 12.3, and 11.4 eV are predicted for the  $\text{XHCO}$  species ( $X = \text{H, F, Cl}$ )

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### **Conformational and energetic properties of the ammonia dimer-comparison of post-hartree-fock and density functional methods (Completo, 1996)**

M. KIENINGER, S. SUHAI

Journal of Computational Chemistry, v.: 17 13, p.:1508 - 1519, 1996

Palabras clave: Métodos de Funcionales de la Densidad Dímero de amoníaco Métodos Post-Hartree-Fock

Areas de conocimiento:

Ciencias Naturales y Exactas / Ciencias Químicas / Físico-Química, Ciencia de los Polímeros,

Electroquímica / Química Teórica y Computacional

Medio de divulgación: Papel

ISSN: 01928651

E-ISSN: 1096987X

The equilibrium structure of the ammonia dimer has been investigated with density functional and MP2 calculations. We used Slater- and Becke-exchange functionals combined with correlation functionals as recommended by Vosko-Wilk-Nusair, by Perdew, and by Lee-Yang-Parr, respectively. The potential energy surfaces was investigated. The asymmetric cyclic "microwave" structure could be identified as a minimum. Optimization of the intermolecular parameters showed that this structure has nearly the same energy as the centrosymmetric cyclic structure. Full optimization transformed the asymmetric cyclic structure into the linear structure. The interaction energies in the dimer were corrected for the basis set superposition error using the Boys-Bernardi counterpoise method and the a priori chemical Hamiltonian approach, respectively.

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**Density functional studies of internal rotation: Formamide as a prototype of the peptide bond (Completo, 1996)**

M. KIENINGER, S. SUHAI

Journal of Molecular Structure, v.: 375 1-2, p.:181 - 188, 1996

Palabras clave: Métodos de Funcionales de la Densidad Enlace peptídico Análisis conformacional

Areas de conocimiento:

Ciencias Naturales y Exactas / Ciencias Químicas / Físico-Química, Ciencia de los Polímeros,

Electroquímica / Química Teórica y Computacional

Medio de divulgación: Papel

E-ISSN: 00222860

Different exchange-correlation potential combinations have been applied to the structural investigation of the planar form of formamide and of its two transition states. The rotational barrier of 18.3 kcal mol<sup>-1</sup> obtained with the Becke3 exchange-Lee, Yang, Parr correlation potential compares well with the MP2 result of 18.7 kcal mol<sup>-1</sup>. The geometrical structure obtained is in good agreement with both MP2 results and experiments.

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**COMPUTER-SIMULATION OF ANTISENSE DNA CONTAINING ENANTIODEOXY-NUCLEOTIDES IN THE DOUBLE HELIX (Completo, 1995)**

M. KIENINGER, S. SUHAI

Anti-Cancer Drug Design, v.: 10 3, p.:189 - 201, 1995

Palabras clave: DNA Antisense DNA Mecánica Molecular Métodos semiempíricos

Areas de conocimiento:

Ciencias Naturales y Exactas / Ciencias Químicas / Físico-Química, Ciencia de los Polímeros,

Electroquímica / Química Teórica y Computacional

Medio de divulgación: Papel

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Computer modeling of DNA double helices containing L-oligo-deoxynucleotides and their complementary D-β-strands in different orientations and conformations was performed using empirical force-field and semiempirical methods. In particular, the parallel and antiparallel orientations of L-α- and L-β-configured strands have been extensively simulated.

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**ULTRAVIOLET STABILIZERS OF THE 2-(2'-HYDROXYPHENYL)-1,3,5-TRIAZINE CLASS - STRUCTURAL AND SPECTROSCOPIC CHARACTERIZATION (Completo, 1995)** Trabajo relevante

G. J. STEUBER, M. KIENINGER, H. SCHETTLER, W. BUSCH, B. GOELLER, J. FRANKEN, H. E. A. KRAMER, H. HOEIER, S. HENKEL, P. FISCHER, H. PORT, T. HIRSCH, G. RYTZ, J.-L. BIRBAUM

The Journal of Physical Chemistry, v.: 99 25, p.:10097 - 10109, 1995

Palabras clave: Espectroscopía UV-Vis Estabilizadores UV

Areas de conocimiento:

Ciencias Naturales y Exactas / Ciencias Químicas / Físico-Química, Ciencia de los Polímeros,

Electroquímica / Química Teórica y Computacional

Medio de divulgación: Papel

ISSN: 00223654

E-ISSN: 15415740

X-ray crystal structure determination of 2,4-diphenyl-6-(2'-hydroxy-4'-methoxyphenyl)-1,3,5-triazine (M-OH-P, Chart 2) reveals a stronger intramolecular hydrogen bond than that in 2-(2'-

hydroxy-5'-methylphenyl)-benzotriazole (Tinuvin P). The O-H distance appears elongated in M-OH-P (0.898 Å), and the H...N distance shortened (1.733 Å), with a definitely more linear hydrogen bond bridge ( $\angle\text{O-H}\cdots\text{N} = 159.6^\circ$ ). IR and  $^1\text{H}$  NMR data confirm this finding ( $\delta\text{OH}\cdots\text{N} = 13.5$  ppm). Both  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra demonstrate the OH bridge to switch from N1 to N5 within the NMR time scale, via rotation around the resorcinyltriazine bond. Derivatives with one aryl group only, e.g. 2-(2'-hydroxyphenyl)-4,6-dimethoxy-1,3,5-triazine (DMH, Chart 1), exhibit a proton-transferred fluorescence with both large Stokes shift (9890  $\text{cm}^{-1}$ ) and high quantum yield ( $\eta\text{F}' = 0.24$ ,  $\lambda_{\text{max}} = 510$  nm, 77 K, methylcyclohexane/2-methylbutane). Introduction of another aryl substituent into the triazine system weakens the proton-transferred fluorescence ( $\zeta\text{F}' \approx 9 \times 10^{-4}$  for 2-(2'-hydroxyphenyl)-4-(dimethylamino)-6-(4'-methylphenyl)-1,3,5-triazine (TN, Chart 1), 77 K). For compounds with three aryl groups, this fluorescence is quenched completely. M-OH-P and 2-(2',4'-dimethoxyphenyl)-4,6-diphenyl-1,3,5-triazine (M-MeO-P, Chart 2; with the bridging hydrogen substituted by a methyl group) display phosphorescence behavior (Table 3) analogous to that of 2,4,6-triphenyl-1,3,5-triazine (TPT, Chart 2). Additionally, a new fluorescence with an exceptionally large and strongly solvent-dependent Stokes shift is observed when the hydrogen of the intramolecular hydrogen bond is replaced by CH<sub>3</sub> (e.g. 2,4-diphenyl-6-(4'-(dodecyloxy)-2'-methoxyphenyl)-1,3,5-triazine (D-MeO-P, Chart 2;  $\Delta\tilde{\nu}_{\text{Stokes}} = 9340$   $\text{cm}^{-1}$ ,  $\eta\text{F} \approx 2.5 \times 10^{-2}$ , AcN, 293 K). For the six OCH<sub>3</sub> derivatives included in this study, the change of dipole moment  $\Delta\mu$  upon excitation has been determined from Lippert-Mataga plots where ( $\tilde{\nu}_{\text{abs}} - \tilde{\nu}_{\text{flu}}$ ) is plotted vs the solvent orientation parameter  $\Delta f$ . Time-resolved emission and viscosity-dependent fluorescence data may be interpreted in terms of a twist between the subunits of D-MeO-P upon excitation

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### THE FO<sub>2</sub> RADICAL - A NEW SUCCESS OF DENSITY-FUNCTIONAL THEORY (Completo, 1995) Trabajo relevante

ON VENTURA, M. KIENINGER

Chemical Physics Letters, v.: 245 4-5, p.:488 - 497, 1995

Palabras clave: Métodos de Funcionales de la Densidad Termoquímica Computacional Óxidos de flúor

Areas de conocimiento:

Ciencias Naturales y Exactas / Ciencias Químicas / Físico-Química, Ciencia de los Polímeros, Electroquímica / Química Teórica y Computacional

Medio de divulgación: Papel

ISSN: 00092614

The structure, heat of reaction and heat of formation of the FO<sub>2</sub> radical in its X<sup>2A</sup> ground state has been calculated using the three-parameter exchange functional of Becke and the Lee-Yang-Parr functional for correlation energy (B3LYP method). B3LYP geometrical parameters of FO<sub>2</sub> and FO are nearer to experiment than those obtained with conventional ab initio calculations. The calculated  $\Delta H_{\text{r},00}$  for  $\text{F} + \text{O}_2 \rightarrow \text{FO}_2$  at this level (-11.1 kcal/mol) is nearer to experiment (-11.68 kcal/mol) than that afforded by any other calculation, including QCISD(T), MP4(SDTQ) or G1 ab initio models. Calculation of the heat of reaction for previously considered isodesmic and isogyric reactions involving the FO<sub>2</sub> radical shows that the agreement is consistent. The root mean square error for the sixteen reactions considered, involving FO, FO<sub>2</sub>, FOH and FOOH, with heats of reaction varying from -149 to +56 kcal/mol, is 0.5 kcal/mol at the B3LYP level. The similar rms error for MP4(SDTQ)/6-311++G(2d, 2p) calculations is 5.2 kcal/mol. It is concluded that the B3LYP method is faster and more accurate than conventional ab initio methods for the study of reactions involving F-O bonds.

Scopus® WEB OF SCIENCE™

### DENSITY-FUNCTIONAL STUDIES ON HYDROGEN-BONDED COMPLEXES (Completo, 1994) Trabajo relevante

M. KIENINGER, S. SUHAI

International Journal of Quantum Chemistry, v.: 52 2, p.:465 - 478, 1994

Palabras clave: Enlaces de hidrógeno Teoría de funcionales de la densidad

Areas de conocimiento:

Ciencias Naturales y Exactas / Ciencias Químicas / Físico-Química, Ciencia de los Polímeros, Electroquímica / Química Teórica y Computacional

Medio de divulgación: Papel

ISSN: 00207608

E-ISSN: 1097461X

Results of density functional calculations will be reported on a variety of hydrogen-bonded complexes, ranging from weak to strong hydrogen bonds. The charged bimolecular NH<sub>3</sub>NH complex and the dimers of water and methanol were investigated using a local approximation of the exchange-correlation potential and two different nonlocal potentials with gradient corrections. In

the case of the water dimers, the dependence of the results on the extension of the atomic basis set has also been investigated. The equilibrium structures of all complexes have been determined. Dipole moments, hydrogen-bond lengths, and hydrogen-bonding energies, calculated with corrections for the basis-set superposition error using the counterpoise method, have been found to agree well with the corresponding experimental result

WEB OF SCIENCE™

#### **THE CHEMICAL HAMILTONIAN APPROACH IN DENSITY-FUNCTIONAL THEORY (Completo, 1994)**

M. KIENINGER , S. SUHAI , I. MAYER

Chemical Physics Letters, v.: 230 6 , p.:485 - 490, 1994

Palabras clave: Teoría de funcionales de la densidad Hamiltoniano químico

Areas de conocimiento:

Ciencias Naturales y Exactas / Ciencias Químicas / Físico-Química, Ciencia de los Polímeros,

Electroquímica / Química Teórica y Computacional

Medio de divulgación: Papel

ISSN: 00092614

The chemical Hamiltonian approach (CHA) for handling the basis set superposition error problem in intermolecular interactions has been implemented within density functional theory (DFT) using Gaussian atomic basis sets. As test examples, the potential curves of the water dimer were calculated using the Vosko-Wilk-Nusair, Becke-Perdew and Perdew exchange-correlation functionals. Comparisons with the counterpoise correction method show that CHA within DFT performs as well as previously for Hartree-Fock.

Scopus® WEB OF SCIENCE™

#### **LIBROS**

##### **New Developments in Quantum Chemistry ( Participación , 2009)**

ON VENTURA , M. E. SEGOVIA , M. P. BADENES , M. KIENINGER , F. BOTTINELLI , K. IRVING

Publicado

Editor/Compilador: José Luis Paz, Antonio J. Hernández

Editorial: Transworld Research Network , Kerala

Areas de conocimiento:

Ciencias Naturales y Exactas / Ciencias Químicas / Físico-Química, Ciencia de los Polímeros,

Electroquímica / Química Teórica y Computacional

Medio de divulgación: Papel

ISSN/ISBN:

Capítulos:

Computational Chemistry Tools for the Study of Environmental Chemistry Problems

Página inicial 109, Página final 164

##### **Kinder entdecken die Naturwissenschaften: Chemie mit 2-3-Jährigen ( Completo , 2008)**

M. KIENINGER Publicado

Número de volúmenes: 1

Número de páginas: 128

Edición: 1

Editorial: Cornelsen Verlag Scriptor GmbH , Berlin

Areas de conocimiento:

Ciencias Naturales y Exactas / Ciencias Químicas / Físico-Química, Ciencia de los Polímeros,

Electroquímica / Experimentos de Química General

Medio de divulgación: Papel

ISSN/ISBN: 3589245581

<http://www.amazon.de/Kinder-entdecken-die-Naturwissenschaften-2-3-J%C3%A4hrigen/dp/3589245581/ref=sr>

##### **Kinder entdecken die Naturwissenschaften: Biologie mit 4-6-Jährigen ( Completo , 2008)**

M. KIENINGER Publicado

Número de volúmenes: 1

Número de páginas: 128

Edición: 1

Editorial: Cornelsen Verlag Scriptor GmbH , Berlin

Areas de conocimiento:

Ciencias Naturales y Exactas / Ciencias Biológicas / Otros Tópicos Biológicos / Experimentos de Biología General

Medio de divulgación: Papel

ISSN/ISBN: 3589245970

<http://www.amazon.de/Kinder-entdecken-die-Naturwissenschaften-4-6-J%C3%A4hrigen/dp/3589245972/ref=sr>

**Kinder entdecken die Naturwissenschaften: Biologie mit 2-3-Jährigen ( Completo , 2008)**

M. KIENINGER Publicado

Número de volúmenes: 1

Número de páginas: 128

Edición: 1

Editorial: Cornelsen Verlag Scriptor Gmbh , Berlin

Areas de conocimiento:

Ciencias Naturales y Exactas / Ciencias Biológicas / Otros Tópicos Biológicos / Experimentos de Biología General

Medio de divulgación: Papel

ISSN/ISBN: 3589245963

<http://www.amazon.de/Kinder-entdecken-die-Naturwissenschaften-2-3-J%C3%A4hrigen/dp/3589245964/ref=sr>

**Kinder entdecken die Naturwissenschaften: Chemie mit 4-6-Jährigen ( Completo , 2008)**

M. KIENINGER Publicado

Número de volúmenes: 1

Número de páginas: 128

Edición: 1

Editorial: Cornelsen Verlag Scriptor Gmbh , Berlin

Areas de conocimiento:

Ciencias Naturales y Exactas / Ciencias Químicas / Química Orgánica / Experimentos de Química General

Medio de divulgación: Papel

ISSN/ISBN: 3589245642

**Kinder entdecken die Naturwissenschaften: Physik mit 2 bis 3-Jährigen: Spaßtage und vieles mehr ( Completo , 2008)**

M. KIENINGER Publicado

Número de volúmenes: 1

Número de páginas: 128

Edición: 1

Editorial: Cornelsen Verlag Scriptor Gmbh , Berlin

Areas de conocimiento:

Ciencias Naturales y Exactas / Ciencias Físicas / Óptica, Acústica / Experimentos de Física General

Medio de divulgación: Papel

ISSN/ISBN: 3589245574

[http://www.amazon.de/Kinder-entdecken-die-Naturwissenschaften-3-J%C3%A4hrigen/dp/3589245573/ref=sr\\_1](http://www.amazon.de/Kinder-entdecken-die-Naturwissenschaften-3-J%C3%A4hrigen/dp/3589245573/ref=sr_1)

**Kinder entdecken die Naturwissenschaften: Physik mit 4 bis 6-Jährigen: Spaßtage und vieles mehr ( Completo , 2008)**

M. KIENINGER Publicado

Número de volúmenes: 1

Número de páginas: 128

Edición: 1

Editorial: Cornelsen Verlag Scriptor Gmbh , Berlin

Areas de conocimiento:

Ciencias Naturales y Exactas / Ciencias Físicas / Óptica, Acústica / Experimentos de Física General

Medio de divulgación: Papel

ISSN/ISBN: 3589245635

<http://www.amazon.de/Kinder-entdecken-die-Naturwissenschaften-6->

**Kinder entdecken die Naturwissenschaften: Technik mit 2 bis 3-Jährigen: Spaßtage und vieles mehr ( Completo , 2008)**

M. KIENINGER Publicado

Número de volúmenes: 1

Número de páginas: 128

Edición: 1

Editorial: Cornelsen Verlag Scriptor Gmbh , Berlin

Areas de conocimiento:

Ingeniería y Tecnología / Otras Ingenierías y Tecnologías / Otras Ingenierías y Tecnologías / Experimentos de Tecnología Común

Medio de divulgación: Papel

ISSN/ISBN: 3589245611

[http://www.amazon.de/Kinder-entdecken-die-Naturwissenschaften-3-](http://www.amazon.de/Kinder-entdecken-die-Naturwissenschaften-3-J%C3%A4hrigen/dp/3589245611/ref=sr_1)

[J%C3%A4hrigen/dp/3589245611/ref=sr\\_1](http://www.amazon.de/Kinder-entdecken-die-Naturwissenschaften-3-J%C3%A4hrigen/dp/3589245611/ref=sr_1)

**Kinder entdecken die Naturwissenschaften. Technik mit 4- bis 6-Jährigen: Spaßtage und vieles mehr! ( Completo , 2008)**

M. KIENINGER Publicado

Número de volúmenes: 1

Número de páginas: 128

Edición: 1

Editorial: Cornelsen Verlag Scriptor Gmbh , Berlin

Areas de conocimiento:

Ingeniería y Tecnología / Otras Ingenierías y Tecnologías / Otras Ingenierías y Tecnologías / Experimentos de Tecnología Común

Medio de divulgación: Papel

ISSN/ISBN: 3589245666

[http://www.amazon.de/Kinder-entdecken-Naturwissenschaften-Technik-6-](http://www.amazon.de/Kinder-entdecken-Naturwissenschaften-Technik-6-J%C3%A4hrigen/dp/3589245662/ref=)

[J%C3%A4hrigen/dp/3589245662/ref=](http://www.amazon.de/Kinder-entdecken-Naturwissenschaften-Technik-6-J%C3%A4hrigen/dp/3589245662/ref=)

**Advances in Quantum Chemistry ( Participación , 1997)**

M. KIENINGER , ON VENTURA , K. IRVING Publicado

Editor/Compilador: PER-OLOV LOWDIN, JOHN R. SABIN, MICHAEL C. ZERNER, JACEK KARWOWSKI, MAT1 KARELSON

Número de volúmenes: 28

Editorial: Academic Press , San Diego

Palabras clave: Radicales Métodos de Funcionales de la Densidad

Areas de conocimiento:

Ciencias Naturales y Exactas / Ciencias Químicas / Físico-Química, Ciencia de los Polímeros, Electroquímica / Química Teórica y Computacional

Medio de divulgación: Papel

ISSN/ISBN: 9780120348282

The application of density functional theory (DFT) to the study of the structure and reactivity of some molecules with unpaired electrons (radicals) performed by our group is presented. The results describe the application of LSD, gradient corrected and hybrid DFT methods to several small molecules. On average the results are as good as highly-correlated post-Hartree-Fock methods, but still some problems remain to be solved

Capítulos:

Density functional theory: A useful tool for the study of free radicals

Página inicial 293, Página final 300

**DOCUMENTOS DE TRABAJO**

**A reinvestigation of the deceptively simple reaction of toluene with  $\cdot\text{OH}$ , and the fate of the benzyl radical. I. A combined thermodynamic and kinetic study on the competition between  $\cdot\text{OH}$  addition and hydrogen abstraction reactions. (2019)**

Completo

M. KIENINGER , Z. SALTA , AM Kosmas , MARC SEGOVIA , VENTURA, O.N. , BARONE, V.

Palabras clave: Toluene hydroxyl radical photodegradation atmospheric chemistry density functional methods

Areas de conocimiento:

Ciencias Naturales y Exactas / Ciencias Químicas / Físico-Química, Ciencia de los Polímeros, Electroquímica / Química Teórica y Computacional

Medio de divulgación: Internet

[https://chemrxiv.org/articles/A\\_Reinvestigation\\_of\\_the\\_Deceptively\\_Simple\\_Reaction\\_of\\_Toluene\\_with\\_C](https://chemrxiv.org/articles/A_Reinvestigation_of_the_Deceptively_Simple_Reaction_of_Toluene_with_C)

This work reports density functional and composite model chemistry calculations performed on the reactions of toluene with the hydroxyl radical. Both experimentally observed H-abstraction from the methyl group and possible additions to the phenyl ring were investigated. Reaction enthalpies and heights of the barriers suggest that H-abstraction is more favorable than OH addition to the ring. The calculated reaction rates at room temperature and the radical-intermediate product fractions support this view. This is somehow contradictory with the fact that, under most experimental conditions, cresols are observed in a larger concentration than benzaldehyde. Since the accepted mechanism for benzaldehyde formation involves H-abstraction, a contradiction arises that begs for an explanation. In this first part of our work we give the evidence that supports the preference of hydrogen abstraction over OH addition and suggest an alternative mechanism which shows that cresols can actually arise also from the former reaction and not only from the latter.

## Producción técnica

### PROCESOS

#### Trabajo Científico CIBA-Geigy (1991)

Proceso Productivo

M. KIENINGER

País: Alemania

Disponibilidad: Restricta

Proceso con aplicación productiva o social

Institución financiadora: CIBA-GEIGY

Areas de conocimiento:

Ciencias Naturales y Exactas / Ciencias Químicas / Físico-Química, Ciencia de los Polímeros, Electroquímica / Química Teórica y Computacional

Medio de divulgación: Papel

### OTRAS PRODUCCIONES

### DESARROLLO DE MATERIAL DIDÁCTICO O DE INSTRUCCIÓN

#### Espectroscopia Computacional (2019)

M. KIENINGER

País: Uruguay

Idioma: Español

Medio divulgación: Internet

Espectroscopia Computacional: Calcular Spectra UV, IR, Raman, ESR, NMR con métodos DFT y DFT

#### metódos DFT y T-DFT (2019)

M. KIENINGER

País: Uruguay

Idioma: Español

Medio divulgación: Internet

mini curso con respecto a métodos en la teoría funcional de la densidad

## Evaluaciones

### EVALUACIÓN DE PUBLICACIONES

### COMITÉ EDITORIAL

## Journal of Physical Chemistry A ( 1998 / 1999 )

Cantidad: Menos de 5

### EVALUACIÓN DE EVENTOS Y CONGRESOS

#### SOIBIO+10 ( 2019 )

Comité programa congreso  
Uruguay

## Formación de RRHH

### TUTORÍAS CONCLUIDAS

#### OTRAS

##### Uso de Hyperchem para modelado molecular de tioles

Iniciación a la investigación  
Sector Educación Superior/Público / Universidad de la República / Facultad de Química , Uruguay  
Nombre del orientado: Paula Tejera  
País: Uruguay  
Palabras Clave: Química computacional pyrazolil borato zinc  
Areas de conocimiento:  
Ciencias Naturales y Exactas / Ciencias Químicas / Físico-Química, Ciencia de los Polímeros,  
Electroquímica / Química Teórica y Computacional  
Colaboración con el Prof. Oscar Ventura en la orientación de la estudiante Paula Tejera, quien iniciara un trabajo de investigación --luego suspendido-- sobre complejos de pyrazolyl borato zinc con diferentes sulfuros.

## Otros datos relevantes

### PREMIOS, HONORES Y TÍTULOS

#### Nature Writing Price (2019)

(Internacional)  
Bund für Naturschutz, Berlin, Alemania  
Trabajo literario-científico sobre problemas medioambientales.

#### Investigador Honorario Grado 3 (2010)

(Nacional)  
Peduciba  
Designación como Investigador Honorario del Área Química del Peduciba. Ver acta en [http://www.peduciba.edu.uy/peduciba/resoluciones/actas/CEN/CEN\\_DIR\\_20100902.pdf](http://www.peduciba.edu.uy/peduciba/resoluciones/actas/CEN/CEN_DIR_20100902.pdf)

#### Feodor-Lynen Stipendium (1998)

(Internacional)  
Alexander von Humboldt-Stiftung  
Beca de investigación para realizar estudios de post-doctorado en Uruguay, concedida por concurso únicamente a ciudadanos alemanes que quieran realizar estadías de investigación en el exterior de Alemania. Se concede únicamente por un año y en casos realmente excepcionales se renueva por otro año consecutivo.

#### Feodor-Lynen Stipendium (1997)

(Internacional)  
Alexander von Humboldt-Stiftung  
Beca de investigación para realizar estudios de post-doctorado en Uruguay, concedida por concurso únicamente a ciudadanos alemanes que quieran realizar estadías de investigación en el exterior de Alemania. Se concede únicamente por un año y en casos realmente excepcionales se

renueva por otro año consecutivo.

## PRESENTACIONES EN EVENTOS

### SOIBIO+10 (2019)

Congreso  
Calculation of the Infrared Spectra in the Open and Closed Structures of the Cofactor Flavin Adenine Dinucleotide (FAD) as the Prerequisite for Studies of Light-Triggered Proton and Electron Transfer  
Uruguay  
Tipo de participación: Expositor oral  
Carga horaria: 20  
Nombre de la institución promotora: Facultad de Química Palabras Clave: FAD IR-Spectra

### 11th congress on electronic structure (2018)

Congreso  
Theoretical study of the initial steps in the reaction of toluene with the hydroxyl radical  
España  
Tipo de participación: Otros  
Carga horaria: 20  
Nombre de la institución promotora: Espa Palabras Clave: Hydroxyl radical theoretical study  
Areas de conocimiento:  
Ciencias Naturales y Exactas / Ciencias Químicas / Ciencias Químicas / química teorica

### XLIII Congrès de Chimistes Theoriciens d'Expression Latine (2017)

Congreso  
Correlation consistent versus polarization consistent optimized basis sets in density functional calculations of halogen oxide species  
Francia  
Tipo de participación: Expositor oral  
Carga horaria: 5  
Nombre de la institución promotora: Quitel Palabras Clave: DFT halogen oxide species  
Areas de conocimiento:  
Ciencias Naturales y Exactas / Ciencias Químicas / Ciencias Químicas / química teorica

### XLIII Congrès de Chimistes Theoriciens d'Expression Latine (2017)

Congreso  
Theoretical exploration of the reaction between sulfenyl and thiol radicals  
Francia  
Tipo de participación: Otros  
Carga horaria: 5  
Nombre de la institución promotora: Quitel Palabras Clave: DFT sulfenyl radical thiol radical  
Areas de conocimiento:  
Ciencias Naturales y Exactas / Ciencias Químicas / Ciencias Químicas / teórica

### Seminario de Físico-Química en América Latina (2013)

Congreso  
Físicoquímica Molecular en Uruguay Desde pequeñas moléculas en química atmosférica a sistemas enzimáticos  
Brasil  
Tipo de participación: Expositor oral  
Carga horaria: 40  
Nombre de la institución promotora: Universidad de Integración Latinoamericana Palabras Clave: Físicoquímica Molecular  
Areas de conocimiento:  
Ciencias Naturales y Exactas / Ciencias Químicas / Físico-Química, Ciencia de los Polímeros, Electroquímica / Química Teórica y Computacional  
Físicoquímica Molecular en Uruguay. Desde pequeñas moléculas en química atmosférica a sistemas enzimáticos Oscar N. Ventura, Kenneth Irving, Martina Kieninger, Patricia Saenz-Méndez, Mauricio Vega, Marc E. Segovia, Aline Katz, Fiorentina Bottinelli, Eduardo Bermúdez Computational Chemistry and Biology Group (CCBG), DETEMA, Facultad de Química, UdelaR, Isidoro de María 1620, Montevideo 11400, Uruguay El CCBG es un grupo de investigación de la Facultad de Química de la Universidad de la República. Nuestros intereses se centran en el uso de métodos de

la química computacional para el estudio de problemas en distintas áreas de la química. En esta presentación se repasará un cierto número de nuestros proyectos, a efectos de potenciar la posible colaboración con otros grupos latinoamericanos. En primer lugar se presentarán estudios sobre óxidos de fluro y cloro, haciendo énfasis en las reacciones de interés en química atmosférica. Algunos de los compuestos clorados tienen interés en las reacciones del ClO<sub>2</sub> con fenoles en el proceso de blanqueado de la celulosa, lo que nos llevará a hablar de reacciones involucradas en la química del procesamiento de la madera. Otros compuestos halogenados tienen interés desde el punto de vista de la contaminación de cursos de agua, y en ese sentido mencionaremos los estudios sobre dioxinas policloradas empleando DFT. Los compuestos fluorados y clorados más simples serán usados como ejemplo de cálculos termodinámicos y cinéticos usando DFT y VTST con una breve mención a nuestras aplicaciones de quantum Monte-Carlo. Presentaremos a continuación estudios de reacciones químicas orgánicas. Se abordarán dos casos, por una parte problemas de combustión relacionados con el óxido de propileno y la oxidación de dobles enlaces empleando H<sub>2</sub>O<sub>2</sub> disuelto en CO<sub>2</sub>, particularmente en relación a monolignoles y derivados. Asimismo, presentaremos reacciones de óxido-reducción de compuestos de azufre, centrándonos en cálculos de calores de formación y reacción química de sulfínos y ácidos sulfénicos. Esto nos llevará a la discusión de las reacciones de peróxido con enzimas como la PTP1B, uno de los ejemplos que presentaremos de sistemas extensos. A continuación se presentarán ejemplos en el área de los biomiméticos, especialmente relacionados con complejos metálicos en centros activos de enzima. Respecto a ello hablaremos de nuestros estudios sobre enzimas, particularmente la BHMT (Betaine homocisteína metil transferasa). Continuaremos hablando luego de otras dos enzimas, la dehaloperoxidasa (especialmente el mecanismo gate de la histidina) y la epóxido hidrolasa microsomal. Finalmente, cerraremos esta revisión de nuestro trabajo hablando de la determinación de espectros IR y Raman en tioles sencillos, complejos de metales de transición y sistemas extensos como los grafenos.

#### **XXXVIII Congrès des Chimistes Theoriciens d'Expression Latine (2012)**

Congreso

Estudio de la reacción de óxido de etileno y óxido de propileno con radicales cloro y oxígeno molecular

Brasil

Tipo de participación: Poster

Carga horaria: 40

Nombre de la institución promotora: Universidade Estadual Paulista, UNESP Palabras Clave: chemical reactivity atmospheric chemistry

Áreas de conocimiento:

Ciencias Naturales y Exactas / Ciencias Químicas / Físico-Química, Ciencia de los Polímeros, Electroquímica / Química Teórica y Computacional

El bromuro de metilo ha sido usado durante muchos años como un potente pesticida. Sin embargo, su efecto sobre la capa de ozono estratosférica ha llevado a la sustitución por otras especies menos agresivas. Uno de los candidatos propuestos es el óxido de propileno (PPO) sobre cuyas reacciones atmosféricas se conoce muy poco. Recientemente se ha estudiado experimentalmente [1] la reacción con radicales cloro en presencia de oxígeno molecular, cuyos pasos iniciales se muestran en la figura a la izquierda. Se identificaron distintos productos de acuerdo a la composición de la mezcla de reacción y, en particular, la preferencia de reactividad de cada hidrógeno en los distintos carbonos de la molécula. Este resultado confirmó estudios previos sobre el óxido de etileno (EO) realizados por FTIR en mezclas O<sub>2</sub>/N<sub>2</sub> [2]. En este trabajo presentamos un estudio detallado del mecanismo de reacción del radical Cl con EO y PPO, realizado con métodos de funcionales de la densidad (BMK) y CCSD(T) con bases 6-31+G(d) y 6-311++G(3df,2pd), así como con modelos químicos (G4 y CBS-QB3). Se estudiaron los caminos alternativos de abstracción de hidrógeno y apertura de ciclo, tanto para EO como PPO, y en el caso de la abstracción, la posterior interacción con oxígeno a través de complejos como el que se muestra a la derecha. Los resultados obtenidos permitieron construir un mecanismo detallado y la determinación de la probabilidad de obtener distintos productos clorados tanto por procesos de adición y apertura de ciclo como por reacciones de terminación de cadena con radicales provenientes del PPO o EO y radicales o moléculas de cloro.

#### **XVI Simpósio Brasileiro de Química Teórica SBQT 2011 Ouro Preto MG, 20-23 Novembro de 2011 30 Anos SBQT (2011)**

Congreso

COMPUTATIONAL STUDY OF THE LIPSCOMB AND LINDSKOG REACTION PATHS FOR HYDROLYTIC Zn ENZYMES

Brasil

Tipo de participación: Otros

Carga horaria: 40

Nombre de la institución promotora: Sociedad Brasileira de Química Teórica Palabras Clave: bioquímica computacional proteínas

Areas de conocimiento:

Ciencias Naturales y Exactas / Ciencias Químicas / Físico-Química, Ciencia de los Polímeros, Electroquímica / Química Teórica y Computacional

El trabajo COMPUTATIONAL STUDY OF THE LIPSCOMB AND LINDSKOG REACTION PATHS FOR HYDROLYTIC Zn ENZYMES, por O. N. Ventura, M. Kieninger (ver <http://www.sbqt.net/palestras/PA10.pdf>) fue presentado en forma oral por el Prof. Ventura como conferencista invitado.

### **9th triennial WATOC Congress (2011)**

Congreso

Computational study of the lipscomb and lindskog reaction paths for hydrolytic Zn enzymes using the L3ZnOH/CS2 biomimetic systems

España

Tipo de participación: Otros

Carga horaria: 40

Nombre de la institución promotora: Universidad de Santiago de Compostela Palabras Clave: bioquímica computacional proteínas

Areas de conocimiento:

Ciencias Naturales y Exactas / Ciencias Químicas / Físico-Química, Ciencia de los Polímeros, Electroquímica / Química Teórica y Computacional

El trabajo "Computational study of the lipscomb and lindskog reaction paths for hydrolytic Zn enzymes using the L3ZnOH/CS2 biomimetic systems" realizado por Paula Tejera, Martina Kieninger y Oscar N. Ventura fue presentado por el Prof. Ventura como conferencista invitado el Jueves 21 de Julio, en el Room C. Ver <http://www.watoc2011.com/index.php/scientific-program>

## **JURADO/INTEGRANTE DE COMISIONES EVALUADORAS DE TRABAJOS ACADÉMICOS**

### **Comisión Evaluadora de trabajos Congreso Soibio (2019)**

Candidato: Varios estudiantes

Tipo Jurado: Otras

M. KIENINGER

Congresos Científicos / Sector Educación Superior/Público / Universidad de la República / Facultad de Química / Uruguay

País: Uruguay

Idioma: Español

Areas de conocimiento:

Ciencias Naturales y Exactas / Ciencias Químicas / Ciencias Químicas / Química Teórica y Computacional

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### PRODUCCIÓN PUBLICADA COMO AUTOR NO CIENTÍFICO

Paralelamente a mi carrera científica, desarrollo una faceta de autor literario con publicaciones en Alemania. El siguiente es un compendio de mi actividad en esta área.

Vom Schreiben auf glatten Oberflächen,

(<http://www.cyberfiction.ch/beluga/digital/99/martina.htm>)

Hyperfictions / Internetliteratur - Die Entwicklung einer deutschsprachigen Netzliteratur

([http://www.amazon.de/Hyperfictions-Internetliteratur-Entwicklung-deutschsprachigen-Netzliteratur/dp/3638712311/ref=sr\\_1\\_22?ie=UTF8&s=books&qid=1258230670&sr=1-22](http://www.amazon.de/Hyperfictions-Internetliteratur-Entwicklung-deutschsprachigen-Netzliteratur/dp/3638712311/ref=sr_1_22?ie=UTF8&s=books&qid=1258230670&sr=1-22))

von Holger Hufer (Compiler), GRIN Verlag; Auflage: 1 (August 2007), ISBN: 978-3638712316

Anatomie des Alltags

([http://www.amazon.de/Anatomie-Alltags-Barbara-E-Geyer/dp/390252555X/ref=sr\\_1\\_1?ie=UTF8&s=books&qid=1258227157&sr=1-1](http://www.amazon.de/Anatomie-Alltags-Barbara-E-Geyer/dp/390252555X/ref=sr_1_1?ie=UTF8&s=books&qid=1258227157&sr=1-1))  
 von Barbara E. Geyer (Autor), Susanne Windelen (Autor), Bodo Hell (Autor), Martina Kieninger (Autor), Cornelia Kolb-Wieczorek (Autor), Bucher GmbH & Co. Druck Verlag Netzwerk; Auflage: 1. Auflage (12. Dezember 2006) ISBN: 978-3902525550  
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 ([http://www.amazon.de/S%C3%A4ngerin-Lampe-Martina-Kieninger/dp/3938743336/ref=sr\\_1\\_13?ie=UTF8&s=books&qid=1258230670&sr=1-13](http://www.amazon.de/S%C3%A4ngerin-Lampe-Martina-Kieninger/dp/3938743336/ref=sr_1_13?ie=UTF8&s=books&qid=1258230670&sr=1-13))  
 von Martina Kieninger (Autor), Keicher, U; Auflage: 1 (8. Dezember 2006), ISBN: 978-3938743331  
 Die Leidensblume von Nattersheim  
 ([http://www.amazon.de/Die-Leidensblume-Nattersheim-Martina-Kieninger/dp/3935890303/ref=sr\\_1\\_2?ie=UTF8&s=books&qid=1258227157&sr=1-2](http://www.amazon.de/Die-Leidensblume-Nattersheim-Martina-Kieninger/dp/3935890303/ref=sr_1_2?ie=UTF8&s=books&qid=1258227157&sr=1-2))  
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 The Famous Sounds of Absolute Wreaders  
 ([http://www.pOes1s.net/en/projects/famous\\_sound\\_of\\_absolute\\_wreaders.html](http://www.pOes1s.net/en/projects/famous_sound_of_absolute_wreaders.html))  
 ORF Kunstradio, Austria, 2003  
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 ([http://www.amazon.de/Desoxyriboli-Versuchsdurchf%C3%BChrung-Martina-Kieninger/dp/3932843398/ref=sr\\_1\\_12?ie=UTF8&s=books&qid=1258227157&sr=1-12](http://www.amazon.de/Desoxyriboli-Versuchsdurchf%C3%BChrung-Martina-Kieninger/dp/3932843398/ref=sr_1_12?ie=UTF8&s=books&qid=1258227157&sr=1-12))  
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 Presente en KATALOG DER DEUTSCHEN NATIONALBIBLIOTEK (Biblioteca Nacional Alemana) <https://portal.d-nb.de/opac.htm?query=Woe%3D130201472&method=simpleSearch>  
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 Zimmer, <http://www.berlinerzimmer.de/eliteratur/hautzinger/hautz1.htm>  
 Miroslav B. Du?ani?: "Lyrik - Lyric - Poezija": 01.12.08 - 01.01.09  
[http://miroslavdusanicyrik.blogspot.com/2008\\_12\\_01\\_archive.html](http://miroslavdusanicyrik.blogspot.com/2008_12_01_archive.html)

## Indicadores de producci3n

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